



## GASES AND METALS



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*AN INTRODUCTION TO THE STUDY OF  
GAS-METAL EQUILIBRIA*

BY

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## AUTHOR'S PREFACE.

THE behaviour of gases and metals in contact with one another is of fundamental importance in many branches of science and industry. Gas-metal equilibria are being studied from many points of view by different groups of workers. The adsorption of gases on metal surfaces is the controlling factor in many catalytic processes, and is also of great importance in the manufacture of all kinds of vacuum devices, such as electric lamps, thermionic valves, and so on. The diffusion of gases in metals, both solid and liquid, and the solubility of gases in metals, determine success or failure in the manufacture of all metallurgical products.

The general principles underlying the equilibria between gases and metals are now generally established, but owing to the diverse nature of the problems which have led to their investigation, the results obtained in different fields are somewhat widely scattered in scientific literature. This book is intended to bring together under one cover the results of research in all these fields, and to emphasise the intimate connection between these different phenomena.

I have made no attempt to deal with the practical application of these principles to metallurgical processes. Nevertheless, I hope that this book, by defining the

fundamental principles and collecting the available data relating to gas-metal equilibria in an accessible form, will be found of help in understanding and solving these problems.

I have been very greatly helped in the preparation of the book by my colleagues, Mr. C. E. Ransley, B.Sc., and Mr. Ivor Jenkins, B.Sc., and am glad of this opportunity of expressing my gratitude to them. My thanks are also due to Mr. C. C. Paterson, Director of the Research Laboratories of the General Electric Co., Ltd., at Wembley, for permission to refer to the results of work carried out there.

37 GRANGE ROAD,  
BUSHEY, 31st December, 1936.

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## CHAPTER I.

### ADSORPTION.

SCHEELE, in 1777, was the first to observe that gases or vapours brought into contact with charcoal combined with it in some way, but could be recovered by the application of heat. The process was given the name of *adsorption* by Bois Reynolds, and although numerous observations of a similar kind were made by others, the subject did not receive serious consideration till nearly 50 years later. The investigations of de Saussure in 1814, and the later work of Graham, Faraday, Chappius, Bunsen, and others, made clear the main phenomena underlying the adsorption of gases by solids. Faraday,<sup>1</sup> in particular, as early as 1833, described experiments on the reactions of hydrogen and oxygen at the surface of platinum plates, and showed a remarkable insight into the mechanism of this catalytic reaction. He believed that the platinum did not itself play any chemical part in the reaction, but that the molecules of the gases, being condensed on its surface, were in far closer proximity to each other, and therefore in a more favourable condition for reaction to occur. He also investigated the "poisoning" effect of carbon monoxide on the catalytic activity of his platinum plates in promoting oxygen-hydrogen combination, and attributed the effect to the presence of an adsorbed film of carbon monoxide, which hindered the adsorption of the other gases. Faraday had practically no proof at the time that his hypothesis was correct, but we have no reason to modify it essentially now, after 100 years. The subject of adsorption of gases by solids, particularly on metal surfaces, received considerable attention

<sup>1</sup> Faraday, *Phil. Trans.*, 1834, 114, 55.

in connection with catalysis. The word catalysis was originated by Berzelius <sup>1</sup> in 1836, in summarising for the Swedish Academy of Sciences the various isolated observations which had been made up to that time. The oxidation of ethyl alcohol to acetic acid in the presence of platinum had been observed by E. Davy <sup>2</sup> in 1820, and the combustion of hydrogen and oxygen on cold platinum by Döbereiner <sup>3</sup> in 1822. The co-ordination of these, and similar observations, by Berzelius, began a systematic study of the subject. The practical value of catalytic reactions in commercial processes gave an impetus to the investigation of related phenomena, and adsorption was recognised as of fundamental importance. Until quite recent times, investigations of adsorption have mainly been directed to the elucidation of catalytic processes. The development of electric lamps, and later of wireless receiving valves involving the production of high vacua, emphasised the importance of adsorption from another aspect. The removal of the last traces of gas from such devices was rendered difficult by the presence of adsorbed layers of gas on the glass walls and metal components. This led to an intense study of adsorption, with a view not only to removing these adsorbed layers, but also to adsorbing the residual gas deliberately on suitable surfaces as a means of attaining the final vacuum. Another direction in which adsorption on metal surfaces is of very practical significance is in connection with atmospheric corrosion, since it would seem clear that any chemical action must be preceded by adsorption of gas on the surface. Comparatively little work has, however, been done on this aspect of the subject.

**Theories of Adsorption.**—Until about 20 years ago the view generally held was little different to that of de Saussure, and it was assumed that the layer of adsorbed gas was of considerable thickness, becoming gradually less dense as the distance from the surface increased.<sup>4</sup> At the actual surface the gas was so condensed as to be almost in the condition of a liquid, with

<sup>1</sup> Berzelius, *Jahr. f. Chemie*, 1836, 15, 237.

<sup>2</sup> E. Davy, *Phil. Trans.*, 1820, 100, 108.

<sup>3</sup> Döbereiner, *Schweigger's J.*, 1822, 34, 91.

<sup>4</sup> See, for example, Bakker, *Z. Phys. Chem.*, 1915, 89, 1 and Eucken, *Ver. deut. Phys. Ges.*, 1914, 16, 345.

a gradual transition to the gas phase. This idea is illustrated in Fig. 1*a*. It was within this layer that the combination and decomposition in catalytic actions took place. In 1915 Langmuir<sup>1</sup> advanced an entirely new theory which indicated that the adsorbed film was in general not more than one molecule in thickness, involving a sharp boundary between the adsorbed layer and the gas phase, as shown in Fig. 1*b*. He was led to this view by a consideration of the lattice structure of metallic crystals, which had just been demonstrated so beautifully by the Braggs. They showed by means of X-rays that all crystals, including the metals, were built up of atoms

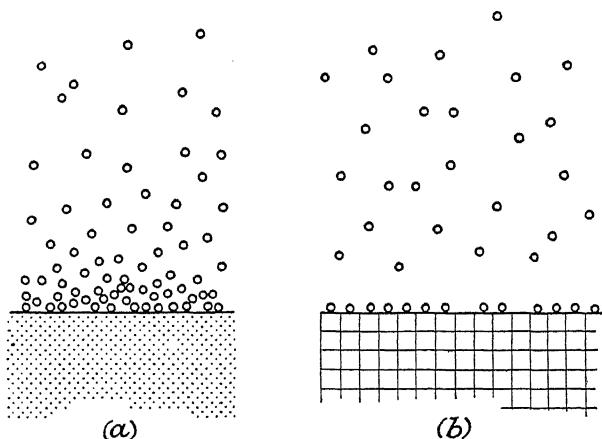


FIG. 1.—Diagram representing (a) old, (b) Langmuir's conception of adsorption.

arranged in a perfectly regular pattern, so that each atom was surrounded by four or more other atoms according to the type of crystal. Each atom was equally bound to its immediate neighbours, and these bonds accounted for the cohesion of the crystal as a whole. Up to this time it had been assumed that crystals were built up of an aggregate of molecules. The fact that in the sodium chloride crystal each sodium atom was found to be surrounded by 6 equidistant chlorine atoms showed

<sup>1</sup> Langmuir, *J. Amer. Chem. Soc.*, 1915, 37, 1165; 1916, 38, 2221; 1917, 39, 1848; 1918, 40, 1361; *Phys. Rev.*, 1916, 8, 149.



that the molecule must have ceased to exist as such in the crystal. Moreover, the forces holding the crystal together could no longer be identified with the ordinary valency bonds, for sodium is monovalent, and yet shared this valency with 6 chlorine atoms. The same thing was found in metal crystals. Copper, silver and gold have a face-centred cubic lattice in which each atom is equidistant from 12 others, and the single chemical valency of these atoms had therefore to be shared between the 12 atoms surrounding it. Reverting again to the sodium chloride crystal, Langmuir points out that when such a crystal is heated till vaporisation occurs, *molecules* of NaCl leave the surface. Since they did not exist in the crystal, the sodium and chlorine atoms must have united at the moment of leaving the surface, and the physical process of evaporation is therefore really indistinguishable from a chemical process. The development of this idea leads to the conclusion that the union of two atoms to form a chemical compound, and the cohesion of molecules to form crystals of a solid are both manifestations of the same kind of attractive force, and that there is no real distinction between physical and chemical attraction. What is usually called chemical combination involves a very strong binding force or primary valency, although the resulting molecule may still have a residual field of force or secondary valency. In the same way, at the surface of any solid crystal there is a layer of atoms in a different state from those in the body of the crystal, in that they are not completely surrounded by other atoms, and have therefore a strong residual valency, or field of attractive force, at the surface. It is this field of force at the surface and the field of force surrounding the gas molecule which causes adsorption to take place when the gas molecule strikes the surface.

Previously it had been assumed that when a gas molecule impinged on the plane surface of a solid it would in general rebound elastically. Langmuir<sup>1</sup> has established that this is not the case, but that a large proportion of the molecules that strike the surface is held there by the intense field of force

<sup>1</sup> Langmuir, *J. Amer. Chem. Soc.*, 1918, 40, 1361.

due to the unsaturated atoms at the surface of the crystal. These condensed molecules subsequently evaporate, and the time they remain on the surface depends on the intensity of the field. Adsorption is therefore due to the balance between condensation and evaporation, and the amount of gas adsorbed depends on the time interval between these two events. If the field of force is weak evaporation takes place so soon after condensation that only a small proportion of the surface is covered at any moment by condensed molecules. When the forces are strong the rate of evaporation may be negligible and the surface will be almost completely covered. In general the maximum adsorption that can be reached represents a layer of gas one molecule thick. The surface forces will then be completely saturated, since it is generally accepted that the attractive force of an atom only extends to a distance of 2 to  $3 \times 10^{-8}$  cm., which is about the distance between the atoms in the lattice. Cases in which adsorbed layers may be more than one molecule thick will be considered later. The experimental results which had led to the view that adsorbed layers were of considerable thickness were probably in error for three reasons. Firstly, the solids used were frequently porous materials whose actual surface was far greater than the apparent surface. Secondly, the use of high pressures and practically saturated vapours led to condensation of liquid in capillary pores. Thirdly, at ordinary temperatures many gases actually diffuse into the interior of the solid, and this solubility was confused with adsorption. Langmuir avoided these difficulties by using large plane surfaces and working at pressures as low as  $10^{-3}$  mm. of mercury, and his classical experiments on the adsorption of gases on mica, glass and platinum established the general truth of his theory.

The surface of a crystal consists of a perfectly regular arrangement of atoms, and in the case of a pure metal all the atoms are of the same kind. There will therefore be a regular arrangement of uniform spaces capable of holding adsorbed molecules, which molecules will also be arranged as a lattice, lying above that of the atoms forming the crystal. The size

of the gas molecules and the spacing of the metal atoms in the crystal will determine whether one or more molecules can be accommodated in each unit space. It is also possible that the molecules may be so large that the number is less than one, a similar condition being familiar to organic chemists as steric hindrance. Some evidence of this has been obtained from electron diffraction patterns (see p. 6).

The total number of molecules adsorbed, or the fraction of the total available spaces occupied, under given conditions of temperature and pressure, depends on the balance between the number of molecules condensed and the rate of evaporation. This depends on the force holding the molecule to the surface and is specific for each gas-metal system. A gas like nitrogen which is relatively inert, or in other words has only a small residual valency, is likely to be less adsorbed than an unsaturated molecule like carbon monoxide. There is also the possibility that the attraction of the metal atoms for the atoms of the gas molecule may be sufficiently great to cause its dissociation, in which case the surface will be covered with adsorbed gas *atoms*. Carrying this process a little further brings us to the case of true chemical combination, as occurs for example when the clean surface of a piece of metallic sodium is exposed to the air. It is therefore clear that every degree of attraction between the surface and gas molecules striking it, and a variety of processes between the simplest form of true adsorption and real chemical combination, may be encountered. This is, of course, in accordance with the observed facts. We will begin by considering the simplest case of adsorption, in which the gas condenses on, and evaporates from the surface as molecules; and we may further simplify it by assuming that each unit space on the surface can accommodate only one molecule.

**The Langmuir Isotherm.**—If there are  $N_0$  spaces per square centimetre, then the maximum possible number of adsorbed molecules will be  $N_0$ , or  $\frac{N_0}{N}$  gram molecules per square centimetre, where  $N$  is Avagadro's constant ( $6.06 \times 10^{23}$  molecules per gram molecule). When equilibrium is established the

rate of evaporation will be  $\nu\theta$ , where  $\nu$  is the rate of evaporation when all the spaces are occupied, and  $\theta$  is the fraction of the surface actually occupied. The rate of condensation, which must equal the rate of evaporation, is given by  $\alpha(1 - \theta)\mu$ , where  $\alpha$  is the fraction of the incident molecules which are condensed (generally nearly equal to unity) and  $\mu$  the number of molecules striking each square centimetre of surface per second.

Since 
$$\alpha(1 - \theta)\mu = \nu\theta,$$
 then 
$$\theta = \frac{\alpha\mu}{\nu + \alpha\mu} \quad . \quad . \quad . \quad . \quad (1)$$

We may put  $\frac{\alpha}{\nu} = k$ , a constant, and the adsorption  $A$ , in gram molecules per square centimetre is given by

$$A = \frac{N_0}{N} \left( \frac{k\mu}{1 + k\mu} \right) \quad . \quad . \quad . \quad . \quad (2)$$

From the kinetic theory

$$\mu = p / \sqrt{2\pi MRT} \quad . \quad . \quad . \quad . \quad (3)$$

where  $M$  is the molecular weight of the gas, and  $\mu$  is therefore proportional to the pressure  $p$ , so that we can write equation (1) in the form

$$\theta = \frac{ap}{1 + ap} \quad . \quad . \quad . \quad . \quad (4)$$

Since the values of  $N_0$  and  $k$  have to be determined empirically, equation (2) may be written <sup>1</sup>

$$x = b \cdot \frac{ap}{1 + ap} \quad . \quad . \quad . \quad . \quad (5)$$

where  $x$  is the adsorption in c.c. per 100 grams, and  $b$  is a constant.

The derivation of the Langmuir adsorption isotherm which has just been given is based on a kinetic argument which balances the rates of deposition and evaporation. Fowler <sup>2</sup> has shown

<sup>1</sup> Taylor, "Physical Chemistry," 2nd edn., 1930, p. 1667.

<sup>2</sup> Fowler, *Proc. Camb. Phil. Soc.*, 1935, 31, 260.



equation (4) is shown in Fig. 2. At very low pressures the equation approximates to  $\theta = ap$ , and adsorption will be proportional to the pressure. At high pressures  $\theta = 1$ , and adsorption becomes independent of pressure, or, in other words, the surface becomes saturated when it is completely covered with a monomolecular layer. At intermediate pressures the equation approximates to  $\theta = ap^{1/n}$ , where  $n$  is greater than one. This form of the equation had previously been proposed by Ostwald, and revived by Freundlich, who found it to hold generally over small ranges of pressure. It is usually referred to as the Freundlich adsorption isotherm. This equation cannot, however, represent the conditions when saturation is

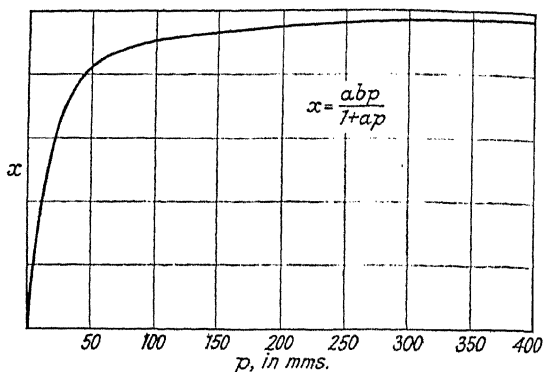


FIG. 2.—The Langmuir adsorption isotherm.

reached, whereas the Langmuir isotherm does so. Experimental results vary with different gas-metal systems, and whilst there is often a definite saturation corresponding to a complete molecular layer, this is not always the case.

With regard to the effect of temperature on adsorption, it is to be noted that the constant  $k$  in equation (2) includes the rate of evaporation, and must therefore be an exponential function of the temperature. So also must the constant  $a$  in equation (5), and we may write

$$a = c \cdot e^{\frac{Q}{RT}} \quad (8)$$

where  $Q$  is the heat of adsorption. The value of  $a$  must also vary as  $1/\sqrt{T}$ , since it includes this relation in equation (3),

although the effect of this may be neglected. Adsorption measurements made at low temperatures usually show decreasing adsorption with increase in temperature, but at higher temperatures adsorption may increase again. This, and other anomalies, indicate that adsorption is not always of the same kind, and at least two types of adsorption, if not more, can be distinguished.

Although there is still considerable divergence of opinion regarding the exact mechanism involved in these different types of adsorption, they can be readily distinguished. The adsorption which is usually observed at low temperatures, e.g. —  $180^{\circ}$  C., is regarded as physical adsorption, in which the gas is adsorbed as molecules and held simply by residual valencies. Whether such adsorption actually occurs on a clean metal surface or on a previously adsorbed layer of gas must be further considered. In this type of adsorption equilibrium is reached very quickly, the heat of adsorption is low, and the amount of gas adsorbed decreases with increase in temperature. The process is, as a rule, completely reversible, and the same values are found whether the equilibrium is approached from one direction or the other. Adsorption of this kind is mainly a property of the surface, and, at saturation, all gases are adsorbed to roughly the same extent. It is sometimes referred to as Van der Waals, or reversible adsorption.<sup>1</sup>

At higher temperatures adsorption of another type may take place. It is almost certain that in this case the molecule is dissociated on adsorption and much more firmly held to the metal surface. This is known as chemi-sorption or irreversible adsorption, and probably involves a definite chemical valency. This type of adsorption is a relatively slow process, several hours being required to reach equilibrium. The heat of adsorption is greater and, over a certain range of temperature, adsorption increases with increase in temperature. It appears that a definite activation energy is required for the

<sup>1</sup> The terms Primary and Secondary adsorption, which are sometimes used, lead to confusion, since physical (primary) adsorption is due to secondary valencies, whilst the slow adsorption which succeeds it (secondary) is due to primary or chemical valencies.

process to occur, and Taylor has suggested the term activated adsorption for this type of slow chemical adsorption. It is further distinguished from physical adsorption by the fact that it is specific and only occurs with certain gas-metal systems. The noble gases, for instance, which have no chemical valencies are only adsorbed at low temperatures, and show no evidence of activated adsorption with any metals.

With this introduction we must now consider the experimental evidence, and return again to the question of how nearly the Langmuir concept gives a true picture of the adsorption processes.

### Experimental.

From what has been said it will be apparent that the study of adsorption is not confined to the determination of isotherms and isobars. The determination of heats of adsorption and rates of adsorption give valuable information. In addition to these direct measurements, the nature of the adsorbed layer can be studied by its effect on other properties of the surface. Both the thermionic and photoelectric properties of surfaces are affected by the presence of adsorbed films. The electron microscope is a new weapon with which these problems are being successfully attacked. Another method, which has been particularly successful in the hands of Roberts, is the determination of the accommodation coefficient, which is very sensitive to the presence of an adsorbed film. A short account of some of the experimental methods may be given, but the reader should consult the original papers to which reference is made, for further details.

Since in general the amount of gas adsorbed is only equivalent to a monomolecular layer on the surface of the adsorbent, special precautions are necessary to obtain accurate results. In the first place it is desirable that the adsorbent should be in such a form that it has the largest possible surface for a given mass, and for this reason most adsorption measurements have been made with metal powders. Whilst this is satisfactory when catalytic processes are under investigation, it is difficult to determine the surface area on which adsorption is taking



place, and such measurements give adsorption in terms of the weight, rather than the surface, of the adsorbent. Adsorption measurements can, however, be made on metals in the form of wire or sheet, the surface area of which is known, by working at low pressures. At pressures of the order of  $10^{-3}$  mm. of mercury it is possible to measure small changes with great accuracy by means of a McLeod gauge, or an ionisation gauge, and adsorption measurements have been made under these conditions on fine wires, although only in a few cases. This technique was first employed by Langmuir<sup>1</sup> in his study of the adsorption of hydrogen, oxygen and carbon monoxide on various surfaces, and similar methods have recently been used by Roberts<sup>2</sup> in adsorption measurements on tungsten filaments. When finely divided metals are used the total adsorption is sufficiently large to enable measurements to be made at higher pressures with accuracy. The experimental method is therefore somewhat different according to whether the adsorbent is in the form of wire or powder.

### Preparation of Metal Powders.

Metal powders are most conveniently prepared by reduction of the powdered oxide in a current of hydrogen. The particle

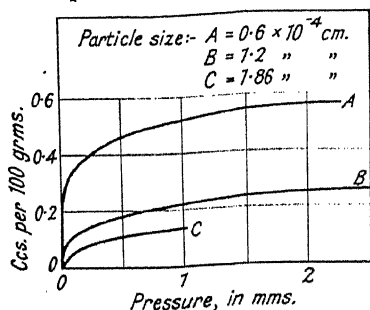


FIG. 3.—Adsorption isotherms for hydrogen on tungsten powder at 180° C.

[Frankenburger and Hodler.

size depends both on the temperature of reduction and on the fineness of the original oxide. The lower the temperature of reduction the finer is the particle size, and therefore the larger is the surface for a given mass. As the temperature is raised the particles grow and sinter together, and the surface area becomes less. This is

illustrated by the three curves in Fig. 3 which show adsorption isotherms for hydrogen on tungsten powders of different particle

<sup>1</sup> Langmuir, *J. Amer. Chem. Soc.*, 1918, 40, 1361.

<sup>2</sup> Roberts, *Proc. Roy. Soc.*, 1935, 152, 445.

size.<sup>1</sup> These particles have a crystalline form and smooth surfaces, so that the surface areas can be calculated with reasonable accuracy. It will be seen that the adsorption varies with the surface area, although not in a perfectly linear manner. The most active adsorbents are obtained by alternate oxidation and reduction, repeated a number of times. Measurements must be confined to temperatures lower than that used in the final reduction, otherwise sintering will take place and the adsorptive power of the material will change during the course of the experiment.

This is shown by Ward's<sup>2</sup> adsorption isotherms for hydrogen on copper in Fig. 4. Curve I relates to a sample reduced and out-gassed at 150° C., whilst Curve 2, for the same sample after further out-gassing at 200° C., shows a reduction of about 30 per cent. in adsorptive power. Taylor and Burns<sup>3</sup> found that the ad-

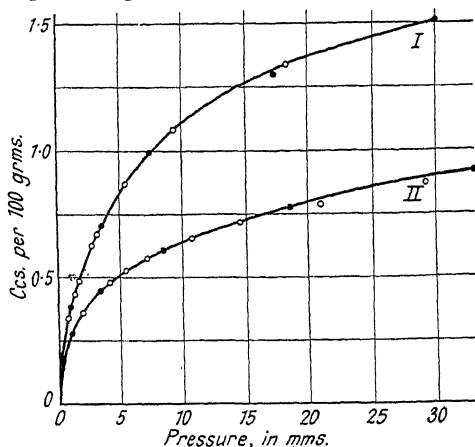


FIG. 4.—Adsorption isotherms for hydrogen on copper powder at 25° C. I. Copper reduced at 150° C. II. After further sintering at 200° C.

[Ward.

isorptive power of nickel reduced at 600° C. was only about 20 per cent. of that found after reduction at 200° C. Provided the temperature at which the adsorbent is finally out-gassed is not exceeded, the adsorptive power remains fairly constant. Very prolonged heating, however, tends to cause sintering and consequent reduction in area. Even when prepared by the same method different samples often show a variation in adsorptive power, and when prepared by different

<sup>1</sup> Frankenburger and Hodler, *Trans. Faraday Soc.*, 1932, 28, 229.

<sup>2</sup> Ward, *Proc. Roy. Soc.*, 1931, 133, 506.

<sup>3</sup> Taylor and Burns, *J. Amer. Chem. Soc.*, 1921, 43, 1273.

methods widely different results are obtained. To obtain reproducible results it is important that the materials should be pure, since it has been found that the presence of impurities may have a marked effect on adsorption.<sup>1</sup>

In most cases the surface area of the adsorbent is not known with any certainty, and adsorptions are therefore usually referred to the weight of the adsorbent. The data presented in this chapter have been calculated on the basis of cubic centimetres of gas at N.T.P. adsorbed by 100 grams of adsorbent. Very different values may therefore appear for the same system due to different methods of preparation, which would show much closer agreement if it had been possible to determine the surface areas. As we shall see later, the surface area alone does not determine the amount of adsorption for a given gas-metal system, but the activity of the surface may be affected by other factors.

The following methods of preparing metal powders are typical of those generally used, and are given by way of illustration.

Copper powder<sup>2</sup> may be prepared by dissolving electrolytic copper in nitric acid, and converting the copper nitrate to oxide by ignition at 300°-400° C. in air. The oxide is then alternately reduced in hydrogen and reoxidised, the temperature of reduction being lowered each time, and the final reduction being carried out at 150° C. At such low temperatures a long time is required for complete reduction, as illustrated by the following schedule which was used by Benton and White :<sup>3</sup>

48 hours at 150° C.  
1 hour „ 170° C.  
10 days „ 115° C.  
9 „ „ 130° C.

Nickel oxide requires a rather higher reduction temperature. Benton and White<sup>4</sup> ignited the nitrate at 400° C. in a muffle

<sup>1</sup> Hurst and Rideal, *J. Chem. Soc.*, 1924, 125, 694.

<sup>2</sup> Ward, *loc. cit.*

<sup>3</sup> Benton and White, *J. Amer. Chem. Soc.*, 1932, 54, 1373.

<sup>4</sup> *Ibid.*, 1930, 52, 2325.

for 17 hours, and then reduced the oxide in hydrogen for 24-hour periods at 200°, 250° and 300° C. Steacie and Stovel<sup>1</sup> used nickel powder that had been reduced in one run of 15 hours at 300° C.

The average particle size of powders prepared by reduction usually lies between  $10^{-3}$  and  $10^{-6}$  cm. The total surface area, assuming the particles to be smooth, will therefore be from  $10^4$  to  $10^7$  cm.<sup>2</sup> per 100 grams of powder. Since the particle diameter changes fairly rapidly with the temperature of reduction it is clear that slight differences in procedure may make enormous differences in the surface area of a given mass. Ward estimated that the surface area of his copper powder, prepared by the method just described, was about  $6 \times 10^4$  cm.<sup>2</sup> per 100 grams, the average particle diameter being  $1.2 \times 10^{-3}$  cm. Adsorption has been studied very largely in connection with catalytic processes, and much of the work on adsorption has consequently been done with materials specially prepared as catalysts. These are often finely divided metals prepared by saturating an inert support with a salt of the metal, which is subsequently reduced in hydrogen. In these cases the surface area of the metal is not known, and adsorption data are only qualitative. Since, however, these materials show particularly strong adsorptive power they facilitate the study of adsorption.

Metal powders should not be exposed to the atmosphere more than necessary after reduction, since they are highly reactive, and the final reduction should take place in the adsorption bulb. After this the surface will be covered with adsorbed hydrogen, and this must be removed by prolonged evacuation at the highest temperature possible without sintering. Many days may be required for the equilibrium pressure to fall to  $10^{-4}$  mm. of mercury, although much shorter periods are often used. As we shall see later, in many cases of activated adsorption the process is not reversible, and the gas is not completely desorbed on lowering the pressure. Burrage<sup>2</sup> has criticised the technique usually employed, and recommends repeated flushing with an inert gas at a high temperature to

<sup>1</sup> Steacie and Stovel, *J. Chem. Phys.*, 1934, 2, 581.

<sup>2</sup> Burrage, *Trans. Faraday Soc.*, 1932, 28, 192.

remove adsorbed films. It is well known to manufacturers of vacuum devices, such as lamps and valves, that adsorbed gases can only be removed with difficulty even at a red heat. Kingdon<sup>1</sup> has shown that an adsorbed film of oxygen is stable on a tungsten surface at temperatures as high as 700° C., and other similar cases are well established. It is therefore highly improbable that the whole of the adsorbed hydrogen is removed by a few hours' evacuation at 150°-300° C., and the equilibrium attained probably represents a definite, but not necessarily clean, surface. The following may be quoted as typical of the de-gassing periods generally used :—

Benton and White<sup>2</sup> for copper, 2 hours at 200° C.

Steacie and Stovel<sup>3</sup> for nickel, 24 hours at 300° C.

Maxted and Moon<sup>4</sup> for platinum black, 12 hours at 100° C.

Roberts<sup>5</sup> believes that an adsorbed film of hydrogen still remains on the surface of the metal no matter how long the evacuation is continued, and that the adsorption usually measured is on this film rather than on clean metal. The evidence for this view will be discussed more fully later (p. 56).

To avoid any possibility of errors due to contaminated surfaces Durau and Teckentrup<sup>6</sup> developed an apparatus for making metal filings in a nitrogen atmosphere, and transferring them directly to the adsorption bulb. With a later arrangement<sup>7</sup> the filing could be carried out in a vacuum. Experiments with copper powders prepared in both ways showed that nitrogen, if adsorbed, is entirely removed by evacuation at room temperature.

### Adsorption Apparatus.

Adsorption measurements usually consist in the determination of the amount of gas adsorbed at different pressures, under

<sup>1</sup> Kingdon, *Phys. Rev.*, 1924, 24, 510.

<sup>2</sup> Benton and White, *J. Amer. Chem. Soc.*, 1932, 54, 1373.

<sup>3</sup> *Loc. cit.*

<sup>4</sup> Maxted and Moon, *Trans. Faraday Soc.*, 1936, 32, 1375.

<sup>5</sup> Roberts, *Proc. Roy. Soc.*, 1935, 152, 445.

<sup>6</sup> Durau and Teckentrup, *Annalen der Physik*, 1932, 12, 927.

<sup>7</sup> Durau and Franssen, *Z. Phys.*, 1934, 89, 757.

constant temperature (isotherms), and the effect of variation in temperature on the amount adsorbed at constant pressure (isobars). The apparatus must therefore be designed so that the temperature of the reaction vessel, the pressure in it, and the total amount of gas introduced can be measured and controlled. Since the changes to be measured are small, care must be exercised, and the precautions customary in high vacuum technique must be observed.<sup>1</sup> Errors due to adsorption on the walls of the apparatus are reduced by keeping the surface as small as possible and capillary tubes are used where possible. Glass taps tend to introduce leaks and should be replaced by mercury cut-offs. Where taps are unavoidable special low vapour pressure grease should be used.<sup>2</sup> Check runs should be made without any adsorbent in the bulb.

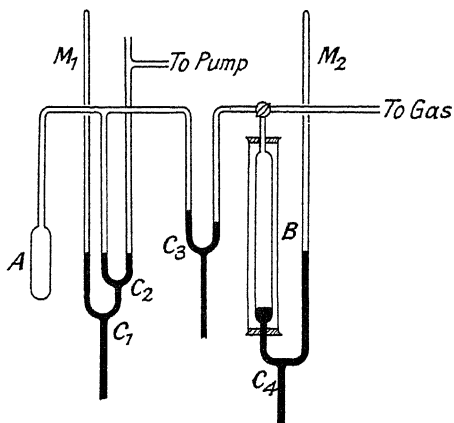


FIG. 5.—Adsorption apparatus.

The type of apparatus generally used is illustrated in Fig. 5.

This form of apparatus was proposed by Pease,<sup>3</sup> and has been modified by Benton and White,<sup>4</sup> and others. It consists of an adsorption bulb A of about 50 c.c. capacity, connected by the mercury cut-off  $C_2$  to a Topley pump, by  $C_1$  to the manometer  $M_1$ , and by  $C_3$  to a tap. This admits gas from a suitable reservoir to a water jacketed measuring cylinder B of known capacity. The volume of the dead space in the adsorption

<sup>1</sup> See, for example, Dunoyer, "Vacuum Practice," 1926, Bell & Sons, and Durau, *Z. Phys.*, 1936, 101, 27.

<sup>2</sup> Such as Apiezon grease manufactured by Shell-Mex Ltd.

<sup>3</sup> Pease, *J. Amer. Chem. Soc.*, 1923, 45, 1197.

<sup>4</sup> Benton and White, *ibid.*, 1930, 52, 2325.

bulb containing the adsorbent can be determined by means of helium, since the noble gases are not adsorbed by metals at atmospheric temperatures. The adsorption determination is then carried out as follows. A measured quantity of gas in the manometer  $M_2$  is passed into the bulb A containing 30-70 grams of the adsorbent. The change in pressure in A with time is then noted until the pressure becomes constant. A further measured quantity of gas is then admitted, and the process repeated until the pressure is practically atmospheric. From the volume of gas admitted and the known volume of the apparatus the volume of gas adsorbed is calculated. To obtain information regarding the reversibility of the adsorption process it is desirable to reverse the procedure and determine the amount of gas desorbed when the pressure is reduced.

Using metal powders prepared as described above, adsorptions of from 1 to 20 c.c. are obtained with 50 grams of metal, and can therefore be measured with fair accuracy. Owing to the uncertainty regarding the actual surface area of the adsorbent when powders are used, it is difficult to determine whether saturation represents the completion of a layer exactly one molecule thick. Information on this point is better obtained by other methods. It may be said, however, that saturation coincides approximately with the completion of a single molecular layer, so far as this can be estimated.

Isobars can be obtained from a series of isotherms determined at various temperatures, by noting the values of adsorption at selected pressures. Here again, however, important information is obtained by studying the reversibility of the process with respect to changes in temperature. Whilst physical adsorption is usually found to be reversible, both with temperature and pressure, chemisorbed gas is not always desorbed when the temperature is changed, and different equilibrium values are obtained when approached from different directions. Since a long time is often required for equilibrium to be reached, a constant temperature is most easily maintained by immersing the adsorption bulb in a bath of suitable boiling-point.

### Heat of Adsorption.

When a gas molecule is adsorbed on a metal surface, heat is given up. This is called the Heat of Adsorption, and its quantitative determination is of importance, since it throws some light on the nature of the binding forces involved. A high heat of adsorption is naturally associated with chemical adsorption, and a lower heat with purely physical adsorption. The heat associated with the adsorption of 1 gram molecule of gas can either be determined directly from measurements of

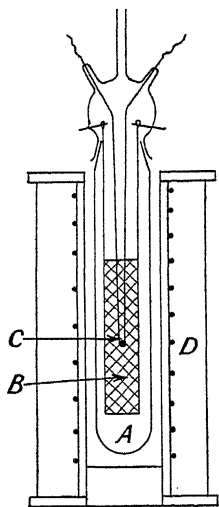


FIG. 6.—Garner's calorimeter. A—adsorption bulb. B—platinum gauze. C—thermocouple. D—furnace.

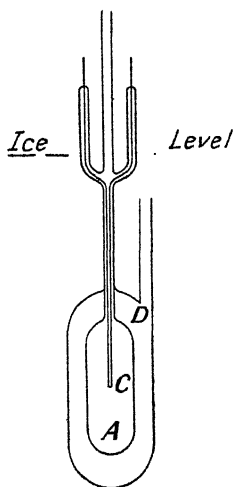


FIG. 7.—Beebe's calorimeter. A—adsorption bulb. C—thermocouple. D—evacuated bulb.

the rise in temperature of the adsorbent, or calculated from the adsorption isotherms.

The total heat of adsorption is usually measured by starting with an evacuated vessel containing the adsorbent, admitting gas to a known pressure, and measuring the rise in temperature by means of a thermocouple and sensitive galvanometer. This gives the mean heat of adsorption for the total quantity adsorbed. There is evidence, however, that the heat of adsorption



may vary as adsorption proceeds, and it is therefore desirable to measure the values for successive additions of small quantities of gas. These values are referred to as the Differential Heats of Adsorption.

The heat of adsorption is usually measured by inserting a thermocouple in the adsorbent and noting the rise in temperature after each addition of gas.<sup>1</sup> The adsorption bulb is enclosed in a constant temperature bath, or in an evacuated vessel to avoid loss of heat, as shown in the arrangements in Figs. 6 and 7.

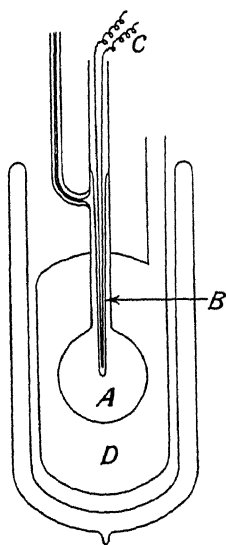


FIG. 8. — Maxted and Moon's calorimeter.  
A—adsorption bulb.  
B—pyrex sheath.  
C—thermocouple.  
D—evacuated bulb.

vessel to avoid loss of heat, as shown in the arrangements in Figs. 6 and 7. Fig. 6 shows Garner's original calorimeter, the adsorbent being contained in the platinum basket B, suspended in the adsorption bulb A. The bulb is surrounded by the furnace D, and the temperature measured by the thermocouple C. Fig. 7 shows a modified form of this apparatus, suitable for use at low temperatures. This apparatus is satisfactory for low gas pressures, but at high pressures heat is conducted rapidly from the thermocouple by the gas. To avoid errors due to this cause, the thermocouple may be protected from direct contact with the gas by a Pyrex sheath. If this is made sufficiently thin, it conducts heat from the adsorbent to the thermocouple satisfactorily. Maxted and Moon<sup>2</sup> used this device in the apparatus shown in Fig. 8. A particularly sensitive micro-

calorimeter which incorporated 30 thermocouples in series was used by Ward<sup>3</sup> to determine the differential heat of adsorption of hydrogen on copper. With this a heat evolution of 0.0005 calories, equivalent to a rise in temperature of 0.00001° C.

<sup>1</sup> Blench and Garner, *J. Chem. Soc.*, 1921, 125, 1288; Maxted, *ibid.*, 1930, 2093; Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, 1930, 34, 799.

<sup>2</sup> Maxted and Moon, *Trans. Faraday Soc.*, 1936, 32, 1375.

<sup>3</sup> Ward, *P. Roy. Soc.*, 1931, 133, 506; *P. Camb. Phil. Soc.*, 1930, 26, 278.

could be detected. It is more usual, however, to calculate the total heat from the isotherms, than to measure it directly. In cases of simple physical adsorption where the process is completely reversible this is reliable, but it is not necessarily so in chemisorption. The methods of calculating heats of adsorption are discussed on page 44.

### Physical Adsorption.

Let us consider first the type of adsorption isotherm obtained at low temperatures—that is in the neighbourhood of

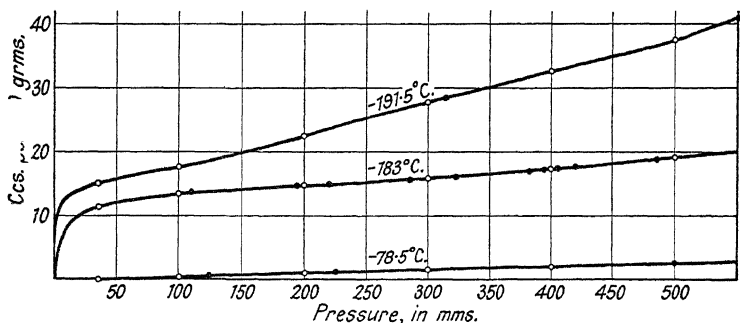


FIG. 9.—Adsorption isotherms for nitrogen on iron reduced at 450° C.  
[Benton.]

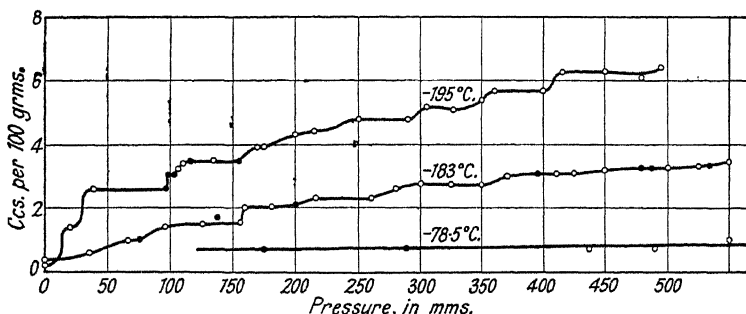


FIG. 10.—Adsorption isotherms for hydrogen on iron reduced at 450° C.  
[Benton.]

—180° C.—in some typical cases. We are indebted to Benton, and Benton and White, for most of the data at very low temperatures. Isotherms for hydrogen, nitrogen, and carbon

monoxide on iron, nickel and copper are given in Figs. 9 to 15. Emmett and Harkness's isotherms for the adsorption of hydrogen by iron at  $-195.8^{\circ}$  and  $-183^{\circ}$  C. are given in Fig. 16. In most cases there is a large adsorption at low pressures, which

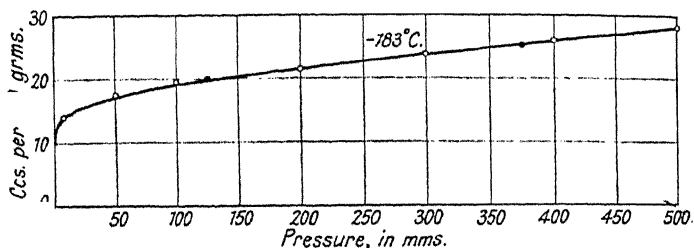


FIG. 11.—Adsorption of CO at  $-183^{\circ}$  C. on iron reduced at  $450^{\circ}$  C.

[Benton.

increases rapidly at first and then more slowly as the pressure is increased. It often happens that the first few admissions of gas are completely adsorbed, and there is no rise in pressure. This is referred to as adsorption at "zero" pressure. Most of

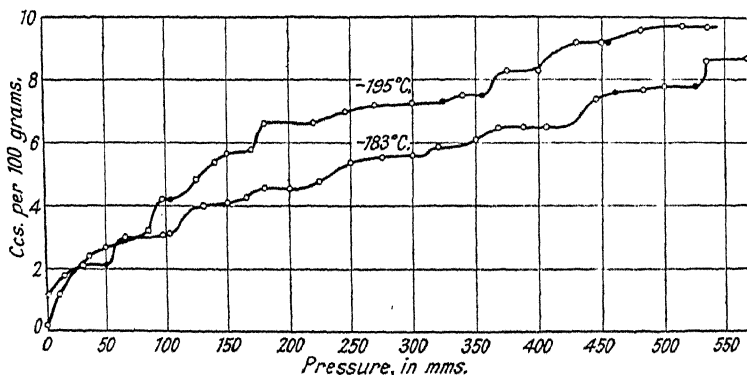


FIG. 12.—Adsorption of hydrogen on copper reduced at  $140^{\circ}$  C.

[Benton.

these curves have the general form of the Langmuir isotherm. As a rule there is no evidence of saturation, although the curves approach an asymptotic value. The Langmuir isotherm may be written

$$x = \frac{abp}{1 + ap},$$

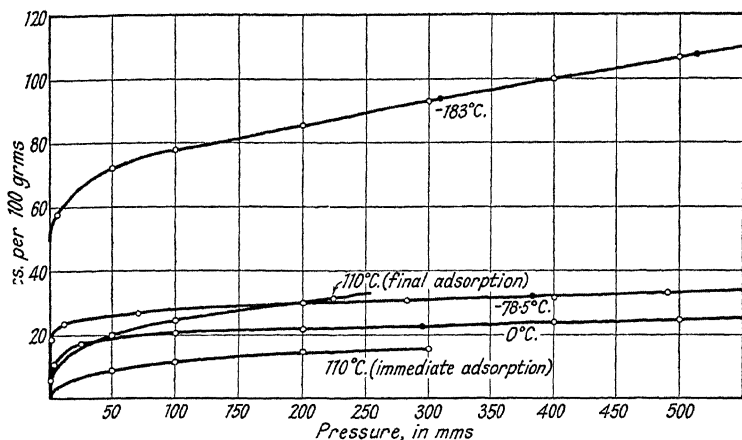


FIG. 13.—Adsorption of CO on copper reduced at 140° C.

[Benton.]

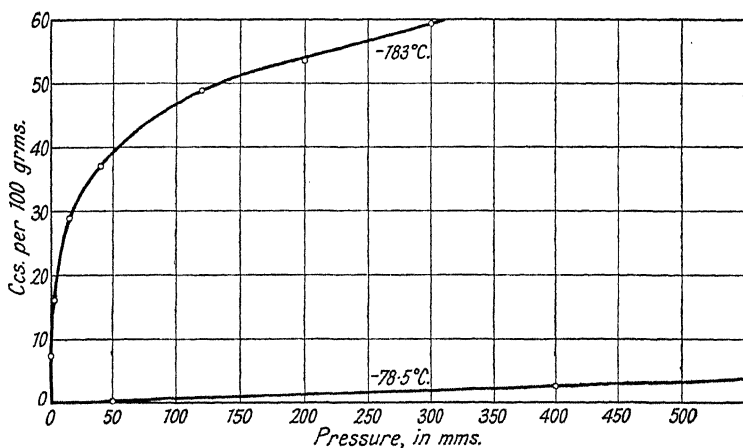


FIG. 14.—Adsorption of nitrogen on copper reduced at 140° C.

[Benton.]

where  $x$  is the amount of gas adsorbed in cubic centimetres per 100 grams of metal, or

$$\frac{p}{x} = \frac{p}{b} + \frac{1}{ab}.$$

If therefore we plot  $p/x$  against  $p$ , we should obtain a straight

line. In Fig. 17 a number of isotherms have been plotted in this way. Whilst some of them show satisfactory agreement

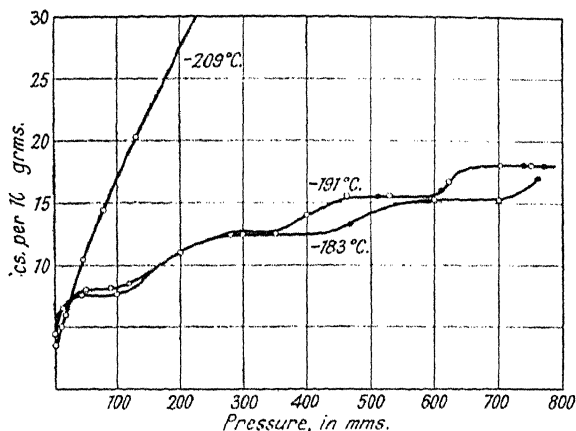


FIG. 15.—Adsorption of hydrogen on reduced nickel.

[Benton and White.

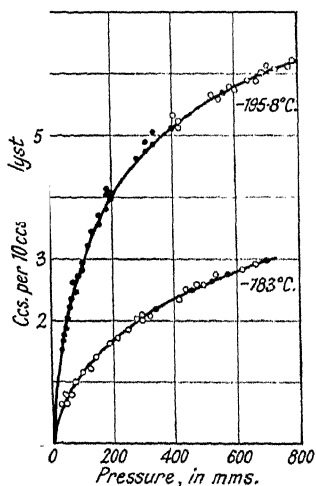


FIG. 16.—Adsorption of hydrogen on a reduced iron catalyst.

[Emmett and Harkness.

with the theoretical equation, this is not always the case. This may to some extent be due to the fact that the process being measured is not one of simple physical adsorption, but that slow adsorption is also occurring. It follows from Langmuir's theory that the time required for half the surface to be covered is less than the mean life of a molecule on the surface. For weak adsorption we should therefore expect equilibrium to be attained very rapidly. This is, in fact, the case, and adsorptions at  $-183^{\circ}\text{C.}$  are almost instantaneous, equilibrium being reached in a few seconds, or at most in one to two minutes. It

is consequently difficult to obtain adsorption-time curves. At higher temperatures, after the first rapid adsorption has taken

place, a further amount is slowly adsorbed. If the sorptions due to the two processes cannot be completely separated, the isotherms will not have the normal form. As a rule, however, this is not difficult, and the isotherm for CO on copper at  $110^{\circ}$  C. in Fig. 13, for example, represents the immediate adsorption only, before the much larger slow adsorption has taken place.

As the temperature is raised, the adsorption at any given pressure is found to be less. This is shown by each of the series of isotherms in Figs. 9 to 16. This would naturally be expected, since adsorption is an exothermic process.

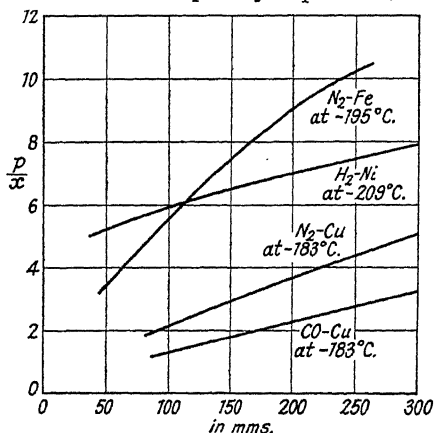


FIG. 17.—Physical adsorption data plotted to check the Langmuir isotherm.

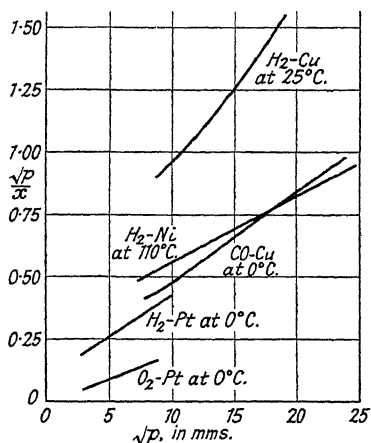


FIG. 18.—Activated adsorption data plotted to check the Langmuir isotherm.

There is not sufficient experimental data to show whether the variation with temperature follows the theoretical equation (5) on page 7, or not. Durau and Tschoepe<sup>1</sup> have been able to show that the adsorption of benzene on crystals of lead chloride accurately obeys this law, and straight lines were obtained by plotting  $\log x$  against  $1/T$ . The effect of temperature may also be shown by plotting the isobars. Benton and White's

<sup>1</sup> Durau and Tschoepe, *Z. Physik*, 1936, 102, 67.

values for hydrogen on copper and nickel are shown in Fig. 19. Similar results found by Emmett and Harkness<sup>1</sup> for hydrogen on iron are plotted in Fig. 20. Where data are available for other systems, they are consistent in showing that physical adsorption decreases with rising temperature. The temperature at which it ceases to be measurable varies with different gas-metal systems. Thus the noble gases, which do not show the slow or activated type of adsorption, are not adsorbed by metals above about  $-80^{\circ}\text{C}$ . Physical adsorption of hydrogen by iron is negligible above  $-100^{\circ}\text{C}$ . Hydrogen is not adsorbed by gold or silver above room temperature, nor nitrogen by copper. On the other hand, physical adsorption of hydrogen by nickel is still appreciable at  $100^{\circ}\text{C}$ .

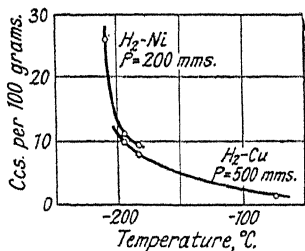


FIG. 19.—Isobars for hydrogen on nickel and copper at low temperatures.

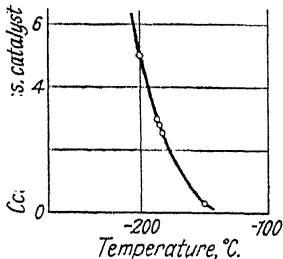


FIG. 20.—Isobar for hydrogen on iron at 760 mm. pressure.

Another characteristic of physical adsorption is the reversible nature of the process. The same values are obtained on approaching equilibrium from either higher or lower pressures. In Figs. 9 to 16 the experimental points obtained by reducing the pressure are marked with heavy dots, and will be seen to lie on the same curves as those marked with open circles which were obtained with increasing pressures. On lowering the pressure after equilibrium has been established, gas is rapidly given up. This affords another proof of the weak nature of the binding forces involved.

At low temperatures all gases are adsorbed by metals, although not to the same extent. Langmuir<sup>2</sup> found that on

<sup>1</sup> Emmett and Harkness, *J. Amer. Chem. Soc.*, 1935, 57, 1631.

<sup>2</sup> Langmuir, *ibid.*, 1918, 40, 1361.

glass and mica, gases showed increasing adsorption in the following order :  $\text{CH}_4$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{Ar}$ , and  $\text{O}_2$ . Benton<sup>1</sup> found that on oxide catalysts gases were adsorbed approximately in the order of their boiling-points, viz.,  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{N}_2$ ,  $\text{O}_2$ , and  $\text{H}_2$ ,  $\text{CO}_2$  being adsorbed most strongly. The following data for adsorption at  $-183^\circ \text{C}$ . and 600 mm. pressure are taken from Figs. 9 to 14 :—

Gas.	Metal.	Adsorption (c.c./100 gms.).
CO	Cu	113
	Fe	31
N <sub>2</sub>	Cu	75
	Fe	21 ✓
H <sub>2</sub>	Cu	10
	Fe	4 ✓

In each case the copper is more active than the iron. It is clear from the data given in this section that physical adsorption is mainly determined by the nature of the surface, and is not specific or selective. This is an important distinction between physical adsorption, which depends only on van der Waals' forces, and adsorption at higher temperatures which depends on chemical valencies.

The weak nature of the binding forces is shown not only by the speed and reversibility of the adsorption process, but also by the low heats of adsorption. Table 1 (p. 28) gives the heats of adsorption determined for a number of systems.

The measured heats are found to vary somewhat with the amount of gas adsorbed and with the previous treatment of the adsorbent. In all cases, however, they are small compared with heats of chemical reaction.

We may therefore summarise the chief characteristics of physical adsorption as follows :—

(a) Adsorption increases with pressure, and approaches an asymptotic value usually representing a layer not exceeding one molecule in thickness.

<sup>1</sup> Benton, *J. Amer. Chem. Soc.*, 1923, 45, 887.



(b) It is not specific. All gases are adsorbed to approximately the same extent, and adsorption depends chiefly on the nature of the surface.

(c) It decreases with increase in temperature, and generally becomes negligible above room temperature.

(d) The process is very rapid, and is completely reversible.

(e) The heat of adsorption is small, and of the order of 2000 calories per gram molecule.

TABLE 1.  
HEATS OF PHYSICAL ADSORPTION.

Metal.	Gas.	Temperature, °C.	Heat of Adsorption, Cals. per gram mol.	Reference.
Copper	Hydrogen	183	400 to 800	1
	Nitrogen	183	3600	1
		78.5	2100	
Iron	Nitrogen	183 } 0 }	2050 to 3700	2
	Hydrogen	195 } 183 }	2000	5
	"	"	1600	2
Silver	Oxygen	183	2000 to 3000	3
Mercury	Krypton	34	2700	4
	Xenon	10	3500	4

It will have been noticed that in some of the low temperature isotherms, particularly those for hydrogen on iron, nickel and copper, in Figs. 10, 12, 15, the experimental points do not lie on a smooth curve. This is a feature of physical adsorption that has not yet received a satisfactory explanation, although it has been observed by a number of workers. It appears that at low temperatures adsorption does not increase steadily as the pressure is increased, but takes place in a series of steps. These steps are very small, and are only apparent when the experimental points are determined at close intervals. It seems

<sup>1</sup> Benton and White, *J. Amer. Chem. Soc.*, 1932, 54, 1373.

<sup>2</sup> Taylor, *Trans. Faraday Soc.*, 1932, 28, 445.

<sup>3</sup> Benton and Drake, *J. Amer. Chem. Soc.*, 1934, 56, 255.

<sup>4</sup> Cassel and Neugebauer, *Z. Phys. Chem.*, 1936, 40, 523.

<sup>5</sup> Emmett and Harkness, *J. Amer. Chem. Soc.*, 1935, 57, 1631.

## ADSORPTION

possible that for this reason they have sometimes been overlooked, or ascribed to experimental error. The fact that the points obtained by desorption lie on the same curves leads to the belief that it is a real effect. Not only has it been observed by Benton and White<sup>1</sup> for hydrogen with several metals, but similar curves have been obtained by Allmand and Burrage<sup>2</sup> for the adsorption of several gases by carbon and silica gel. It is further established that these steps cannot be due to the formation of successive layers, since the adsorptions shown in the figures mentioned represent less than one complete layer in each case. Benton and White<sup>3</sup> have explained these discontinuities by assuming the formation of successive rows of adsorbed molecules, starting at the edges of crystals and proceeding inwards till each face is completely covered. Such a mechanism is only possible if the molecules can migrate over the surface after adsorption. The completion of each row produces a step, the next row being associated with a slightly lower heat of adsorption. These discontinuities would be satisfactorily explained if for any reason different areas of the adsorbent exhibited differences in attraction for the gas molecules. The Langmuir isotherm assumes a uniform surface. If, however, the surface was of two kinds, although the rate of arrival on equal areas would be the same for both, the rates of evaporation (and the heats of adsorption) would be different. One kind of surface would therefore be completely covered before the other, and a discontinuity would result. There is no evidence that similar discontinuities occur in chemical adsorption. This may be explained by the absence of surface migration, or by the fact that for chemical adsorption the surface is uniformly active.

### Activated Adsorption and Chemisorption.

So far we have considered only the experimental results at low temperatures, and seen that adsorption decreases with

<sup>1</sup> Benton and White, *J. Amer. Chem. Soc.*, 1931, 53, 3301.

<sup>2</sup> Allmand and Burrage, *Proc. Roy. Soc.*, 1931, 130, 610; *J. Phys. Chem.*, 1931, 35, 1692; Allmand, Burrage and Chaplin, *Trans. Faraday Soc.*, 1932, 28, 218.

<sup>3</sup> Benton and White, *J. Amer. Chem. Soc.*, 1931, 53, 2807

increasing temperature. As the temperature is raised still further we find, in many cases, that after the initial instantaneous adsorption is complete a further quantity of gas continues to be adsorbed very slowly. This slow adsorption increases at higher temperatures, and after passing through a maximum falls off once more. It is important to note that this type of adsorption is specific, and although very general, does not occur with all gases and all metals. For example, the noble gases do not show activated adsorption. Neither helium nor argon<sup>1</sup> are adsorbed by any metal at temperatures above about  $-78^{\circ}\text{C}$ . Nitrogen is only adsorbed by copper below room temperature,<sup>1</sup> and hydrogen does not appear to be adsorbed by either gold<sup>2</sup> or silver<sup>3</sup> at ordinary temperatures. It would appear, therefore, that this type of adsorption depends on a chemical attraction between the metal surface and the gas, and is most strongly marked in such systems as oxygen-silver, carbon monoxide-nickel, and hydrogen with copper, nickel or iron. It has commonly been called chemisorption, implying a binding force of a chemical nature, that is, by a valency or by the sharing of an electron. Benton<sup>4</sup> first suggested that this represented a second type of adsorption, and that the gas was no longer adsorbed as molecules, but was dissociated at the surface. Langmuir<sup>5</sup> had already indicated that adsorption of this kind was to be expected. Although it cannot actually be chemical combination, since no new phase is formed, it is probably a necessary preliminary to chemical action which may occur at still higher temperatures. In the systems just mentioned, for example, definite compounds  $\text{Ag}_2\text{O}$ ,  $\text{Ni}(\text{CO})_4$ ,  $\text{NiH}_2$ , etc., between gas and metal are known.

Taylor<sup>6</sup> emphasised the importance of the rate of adsorption as indicating that a definite energy of activation was necessary for the process to take place, and suggested the term Activated Adsorption. Since adsorption is always an

<sup>1</sup> Benton and White, *J. Amer. Chem. Soc.*, 1932, 54, 1373.

<sup>2</sup> Benton and Elgin, *ibid.*, 1927, 49, 2426.

<sup>3</sup> *Ibid.*, 1926, 48, 3027.

<sup>4</sup> Benton, *ibid.*, 1923, 45, 887.

<sup>5</sup> Langmuir, *ibid.*, 1918, 40, 1361.

<sup>6</sup> H. S. Taylor, *ibid.*, 1931, 53, 578.

exothermic process it must decrease as the temperature is raised, and the observed increase in the total adsorption at higher temperatures can only be logically explained on the assumption that a second process has begun. Very strong evidence for this was obtained by Taylor and Williamson<sup>1</sup> from a study of the adsorption of hydrogen on a manganous oxide-chromic oxide catalyst. They obtained the isobar shown in Fig. 21, which clearly indicates two adsorption processes. At  $-74^{\circ}\text{C}$ . the heat of adsorption was found to be 1900 cal./gm. mol., and equilibrium was attained in a few minutes. At  $0^{\circ}\text{C}$ . rapid adsorption was followed by a slow increase, indicating

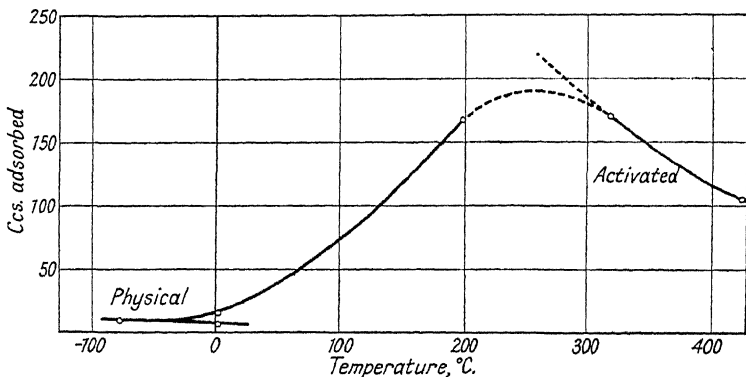


FIG. 21.—Isobar for hydrogen on a manganous oxide-chromic oxide catalyst at 165 mm. pressure.

[Taylor and Williamson.

the beginning of an activated adsorption, which continued to increase over a range of several hundred degrees. At  $300^{\circ}\text{C}$ . the heat of adsorption was nearly 20,000 calories. Taylor concludes that the results represent two processes indicated by the two isobars, with an intermediate range where both occur, but where, owing to the low temperature, activated adsorption does not reach equilibrium in a measurable time.

Similar isobars have been found in many cases for the adsorption of gases by metals. Benton and White<sup>2</sup> found the

<sup>1</sup> Taylor and Williamson, *J. Amer. Chem. Soc.*, 1931, 53, 2168.

<sup>2</sup> Benton and White, *ibid.*, 1930, 52, 2325.

isobars shown in Fig. 22 for the adsorption of hydrogen by nickel. These are of the same form as the one just considered.

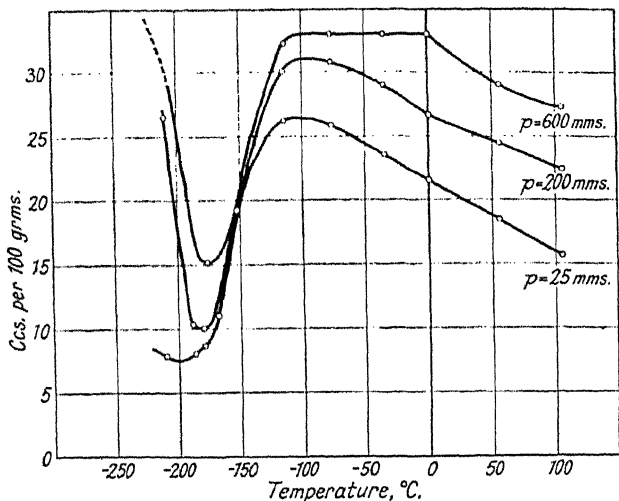


FIG. 22.—Isobar for hydrogen on nickel at different pressures.

[Benton and White.

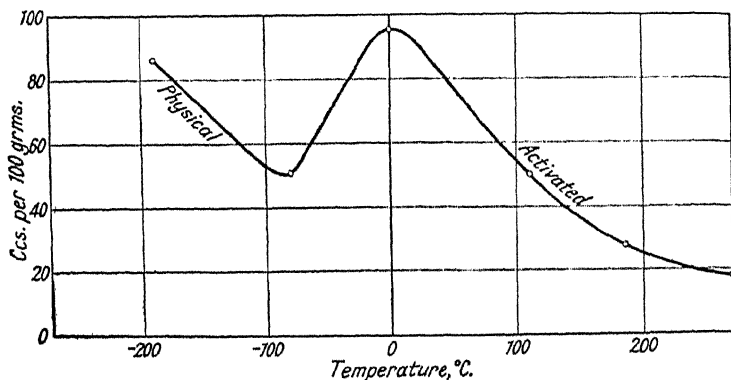


FIG. 23.—Isobar for CO on palladium at 150 mm. pressure.

[Taylor and McKimney.

The adsorptions at  $-205^{\circ}$  C. were much larger than those at  $-180^{\circ}$  C. and equilibrium was reached instantaneously. At  $-100^{\circ}$  C., however, about 1 to 2 hours were required to

reach equilibrium and the total adsorption was more than twice that found at  $-180^{\circ}\text{C}$ . The isobar for a pressure of 600 mm. shows a constant value over a range of about  $100^{\circ}\text{C}$ ., presumably indicating that the surface is completely covered. Above  $0^{\circ}\text{C}$ . adsorption falls steadily as the temperature is increased. Similar isobars have been obtained by Taylor and McKinney<sup>1</sup> for the adsorption of carbon monoxide by palladium (Fig. 23), by Frankenburg and Hodler<sup>2</sup> for ammonia on tungsten powder (Fig. 24), and by Benton and White<sup>3</sup> for hydrogen on copper. By noting the values of

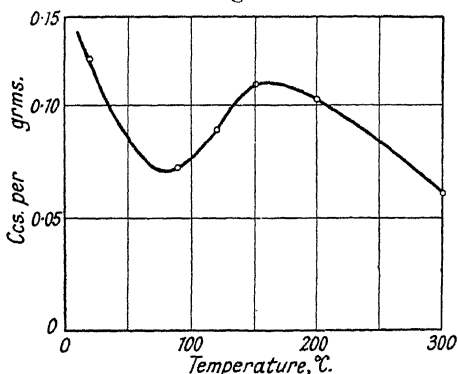


FIG. 24.—Isobar for ammonia on tungsten at 0.5 mm. pressure.

[Frankenburg and Hodler.

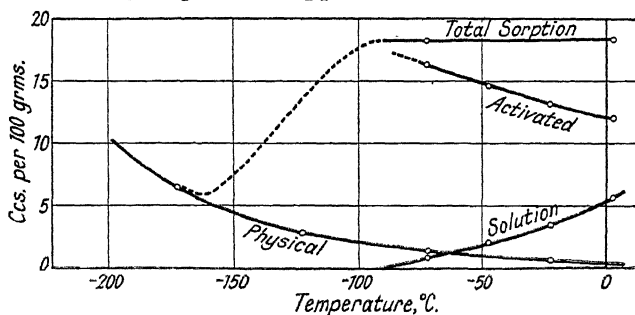


FIG. 25.—Isobar for hydrogen on copper at 500 mm. pressure.

[Benton and White.

instantaneous adsorption as well as the final values for total

<sup>1</sup> Taylor and McKinney, *J. Amer. Chem. Soc.*, 1931, 53, 3604.

<sup>2</sup> Frankenburg and Hodler, *Trans. Faraday Soc.*, 1932, 28, 229. In a later paper (*Naturwiss.*, 1935, 23, 609) the hump in the curve is attributed to the effect of impurities on the surface.

<sup>3</sup> Benton and White, *J. Amer. Chem. Soc.*, 1932, 54, 1373.

adsorption the isobars for the two processes can be drawn separately as in Fig. 25. Benton and White found a similar

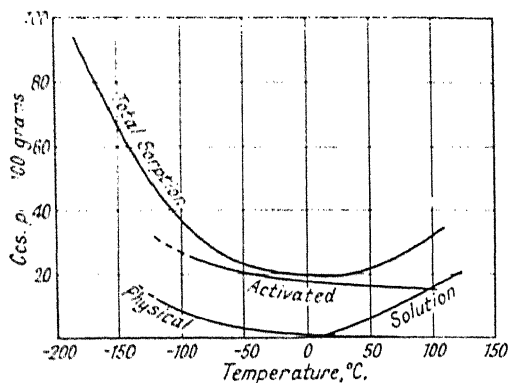


FIG. 26. Isobar for CO on copper at 300 mm. pressure.  
[Benton,

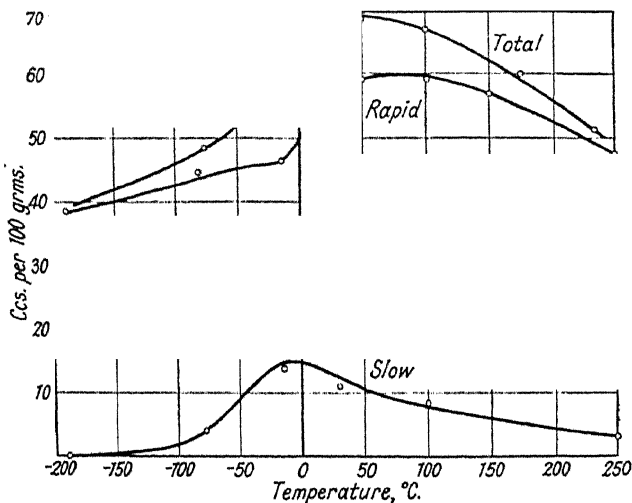


FIG. 27.—Isobar for hydrogen on nickel at 760 mm. pressure.  
[Maxted and Hassid.

result for CO on copper (Fig. 26), although here the physical adsorption was still measurable at 200° C. Maxted and

Hassid's results for hydrogen on nickel, shown in Fig. 27, are exceptional in showing a maximum for both types at

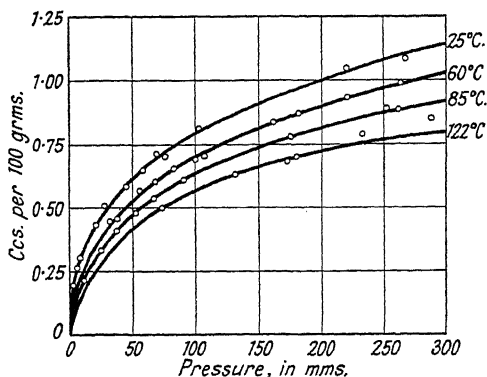


FIG. 28.—Adsorption of hydrogen on copper reduced at 150° C.  
[Ward.]

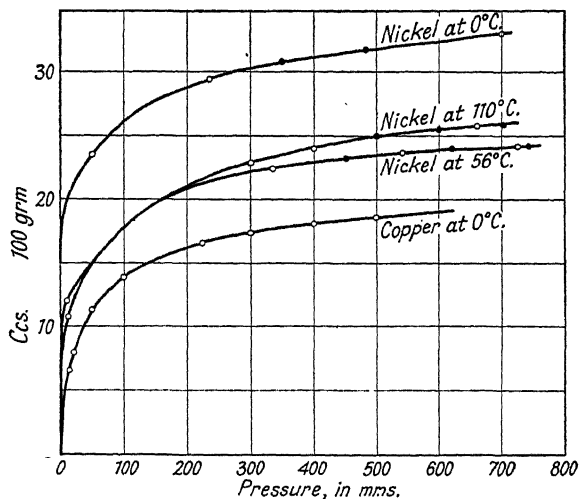


FIG. 29.—Adsorption of hydrogen on nickel and copper.  
[Benton and White.]

50° C., but confirm Benton's results at higher temperatures. In this case the slow process required 3 hours to reach equilibrium.



In general, the rate at which equilibrium is reached increases with increase in both temperature and pressure. Thus Benton and Elgin<sup>1</sup> found a steady increase in the rate at which oxygen was adsorbed by silver as the temperature was raised, and Insley<sup>2</sup> found that hydrogen was adsorbed by nickel more rapidly at 100° C. than at 50° C.

The shape of the isotherms is generally similar to that found with physical adsorption. Some typical examples are seen in Figs. 28 to 33. If the molecules are dissociated and

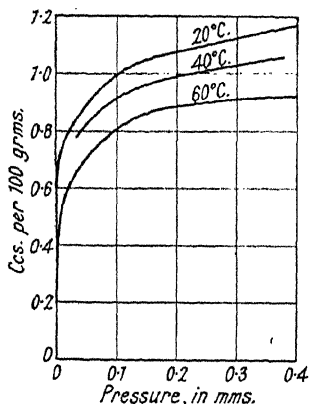


FIG. 30.—Adsorption of ammonia on tungsten powder.

[Frankenburger and Hodler.

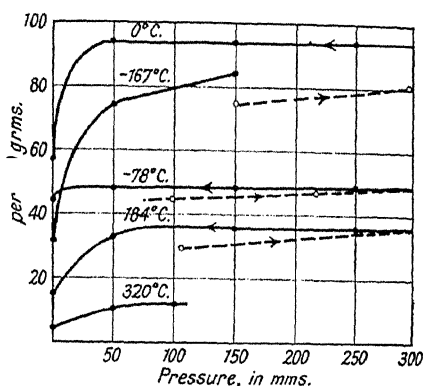


FIG. 31.—Adsorption of CO on palladium.

[Taylor and McKimney.

adsorbed on the surface as atoms the Langmuir isotherm will have the form

$$x = \frac{abp^{\frac{1}{2}}}{1 + ap^{\frac{1}{2}}}$$

and

$$\frac{p^{\frac{1}{2}}}{x} = \frac{1}{ab} + \frac{1}{a}$$

so that straight lines should result when  $\sqrt{p}/x$  is plotted against  $\sqrt{p}$ . Some experimental isotherms conform to this law, as seen in Fig. 18, in others the amount adsorbed is more nearly

<sup>1</sup> Benton and Elgin, *J. Amer. Chem. Soc.*, 1927, 49, 2426.

<sup>2</sup> Insley, *J. Phys. Chem.*, 1935, 39, 623.

proportional to the pressure. Ward found that his results for hydrogen on copper were equally well represented by

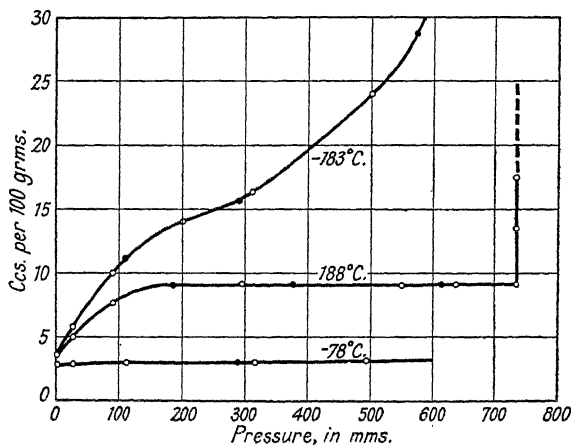


FIG. 32.—Adsorption of oxygen by silver.

[Benton and Drake.]

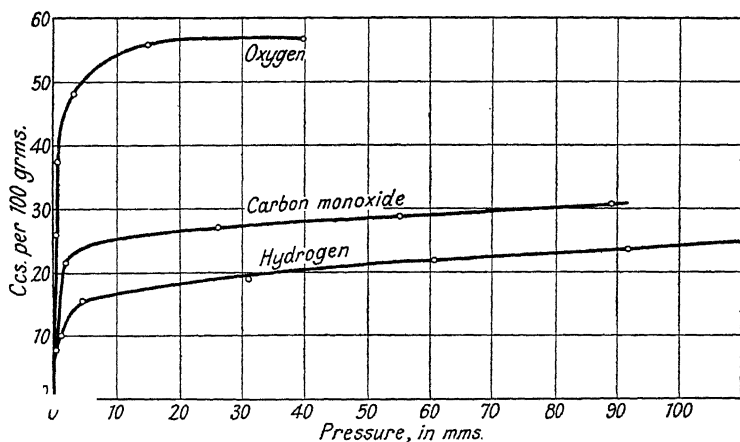


FIG. 33.—Adsorption of gases on platinum black at 0° C.

[Taylor, Kistiakowsky and Perry.]

assuming that adsorption was proportional to the square root of the pressure. It is doubtful whether the experimental results are sufficiently accurate to distinguish between these

different equations. The Freundlich isotherm is generally applicable when a suitable value is chosen for the exponential.

Whilst the process of physical adsorption is perfectly reversible with respect to changes in temperature and pressure, this is not the case with activated adsorption. So far as pressure changes are concerned, the isotherms usually show reversibility, although this is not always so. Benton and White's isotherms for hydrogen on nickel at 0° C., 56.5° C., and 110° C. in Fig. 29 show complete reversibility. This is confirmed by Insley's<sup>1</sup> isotherm at 99.6° C. shown in Fig. 34. Benton and Drake's isotherms for activated adsorption of oxygen by silver at -78° C. and 188° C. also show complete reversibility with

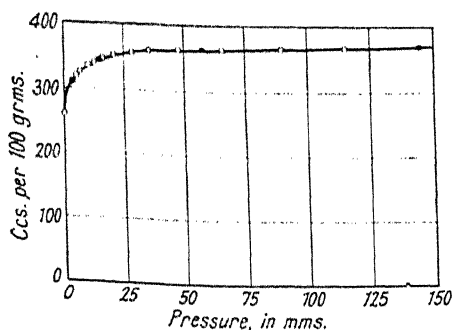


FIG. 34.—Adsorption of hydrogen on nickel at 99.6° C.

[Insley.

pressure. A similar result was obtained by Ward for hydrogen and copper between 25° C. and 122° C., as seen in Fig. 28. On the other hand, Taylor and McKinney found that in the case of hydrogen and palladium the adsorption became

less reversible as the temperature was increased, and higher values were obtained when equilibrium was approached by desorption. Langmuir and Kingdon<sup>3</sup> have shown that oxygen adsorbed on tungsten can only be removed by evacuation above 1200° C. Roberts<sup>4</sup> has obtained similar evidence in the case of hydrogen adsorbed on a clean tungsten surface, although here desorption begins at about 400° C. Durau and Franssen<sup>5</sup> found that at pressures below 1 mm. H<sub>2</sub>, N<sub>2</sub>, and

<sup>1</sup> Insley, *J. Phys. Chem.*, 1935, 39, 623.

<sup>2</sup> Taylor and McKinney, *J. Amer. Chem. Soc.*, 1931, 53, 3604.

<sup>3</sup> Langmuir and Kingdon, *Phys. Rev.*, 1924, 23, 774.

<sup>4</sup> Roberts, *Proc. Roy. Soc.*, 1935, 152, 445.

<sup>5</sup> Durau and Franssen, *Z. Physik*, 1934, 89, 757.

CO are not appreciably adsorbed by copper powder prepared by abrasion in vacuo, but that oxygen and CO<sub>2</sub> are actively adsorbed, and cannot be pumped away.

It appears, therefore, that when the binding force is weak the gas is desorbed on reducing the pressure, but when strong adsorption occurs desorption is so slow that the process is virtually irreversible.

Activated adsorption is never reversible with respect to changes in temperature. If the equilibrium value is found by admitting gas to the adsorbent at a temperature  $T_1$ , and it is then heated, still in contact with the gas, to a higher temperature  $T_2$ , on again cooling to  $T_1$  the equilibrium value is higher than before. Benton and White found that hydrogen adsorbed by nickel at 0° C. was not desorbed on cooling to - 180° C. They conclude, therefore, that an additional physical adsorption takes place on top of the layer chemisorbed at 0° C. Insley<sup>1</sup> confirmed this using a nickel catalyst prepared from the amalgam, and found a 10 per cent. increase in adsorption on cooling from 100° C. to - 80° C., the normal adsorption being repeated on heating again to 100° C. The same system was studied in detail by Maxted and Hassid.<sup>2</sup> They determined the additional adsorption at  $T_1$ , which resulted after heating to  $T_2$ , and again cooling to  $T_1$ . Some of their values are recorded in Table 2.

TABLE 2.

$T_1$ . °C.	Normal Value at $T_1$ . $x_1$ .	$T_2$ . °C.	Normal Value at $T_2$ . $x_2$ .	Final Value at $T_1$ .	$x_1 + x_2$ .
- 190	2.70	0	4.78	7.27	7.48
- 79	3.84	100	5.09	6.34	8.93
- 190	2.70	100	5.09	7.97	7.79

Similar results were obtained with hydrogen and platinum. It is significant that the gas adsorbed as the result of thermal

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Maxted and Hassid, *J. Chem. Soc.*, 1931, 3313.

activation could not be removed by evacuation at  $T_1$ , but only at higher temperatures. This is, of course, in accordance with the usual practice of baking during evacuation to remove gas adsorbed on glass and metal parts of vacuum apparatus.

The effects discussed have been observed with many other gas-metal systems. Benton and White found with hydrogen and copper that if, after establishing equilibrium at  $-78^\circ \text{C}$ ., the temperature was quickly raised to  $0^\circ \text{C}$ . there was an evolution of gas, which was slowly re-adsorbed. On cooling again to  $-78^\circ \text{C}$ . a further adsorption occurred, and this physically adsorbed gas was evolved on again heating to  $0^\circ \text{C}$ . Frankenburg and Hodler<sup>1</sup> found that the adsorption of hydrogen by tungsten powder increased as the temperature was raised from  $20^\circ \text{C}$ . to  $600^\circ \text{C}$ ., but the gas was not desorbed on lowering the temperature again. Steacie and Stovel<sup>2</sup> obtained similar evidence for ethylene and nickel. The quantities of gas adsorbed in each way as the temperature was raised are given in Table 3.

TABLE 3.  
ADSORPTION OF ETHYLENE BY NICKEL.

Temperature, $^\circ \text{C}$ .	Physical Adsorption, c.c.	Activated Adsorption, c.c.
$-80$	5.5	nil
0	1.33	1.56
20	0.81	1.16
50	0.46	0.90
142	nil	7.83

On reducing the temperature from  $142^\circ \text{C}$ . to  $-80^\circ \text{C}$ ., the total adsorption was 12.39 c.c. This is almost exactly equal to the activated adsorption at  $142^\circ \text{C}$ . plus the normal physical adsorption at  $-80^\circ \text{C}$ .

These facts give convincing evidence that two types of adsorption take place. Whilst gas physically adsorbed at low

<sup>1</sup> Frankenburg and Hodler, *Trans. Faraday Soc.*, 1932, 28, 229.

<sup>2</sup> Steacie and Stovel, *J. Chem. Phys.*, 1934, 2, 581.

temperatures may be readsorbed in the activated form at higher temperatures, the reverse change does not apparently take place owing to the strong binding forces involved, and the very slow rate of this process at low temperatures. It also seems clear that a layer of molecular gas may be held by physical adsorption on top of a chemisorbed layer.

The characteristic slow rate of activated adsorption has led to the suggestion that the process is, in fact, one of solution in the metal, and not adsorption on the surface. This view was very strongly supported by Ward,<sup>1</sup> Steacie,<sup>2</sup> and others. It was argued that the irreversible nature of the process lent strong support to this view, since the adsorbed gas was unable to escape from the metal when the temperature was reduced. It is, however, difficult to reconcile this explanation with the known solubilities of the gases, as determined by direct measurement. Moreover, whilst the solubilities are generally of the order of 1-10 c.c. per 100 grams for solid metals, the quantities adsorbed by metal powders are 10-100 times as great, and activated adsorption is observed at temperatures far below those at which any measurable solubility can be found. There are several examples of activated adsorption where solubility can be excluded, as for example with active oxide catalysts, or with gases like ethylene on metal powders. It is probable that at higher temperatures solubility also occurs. Sometimes a relatively rapid activated adsorption is followed by a slower sorption, which may be ascribed to solubility. Where it is difficult to believe that solution can be occurring, it has been suggested that a second type of activated adsorption is taking place. Emmett and Harkness<sup>3</sup> found the isobar shown in Fig. 35 for hydrogen on an iron catalyst. The curve A represents physical adsorption, whilst B and C are considered to be two kinds of activated adsorption having different activation energies.

Ward attributes the slow sorption of hydrogen by copper to solubility. If solution occurs, the rate of diffusion into

<sup>1</sup> Ward, *Proc. Roy. Soc.*, 1931, **133**, 522.

<sup>2</sup> Steacie, *J. Phys. Chem.*, 1931, **35**, 2112.

<sup>3</sup> Emmett and Harkness, *J. Amer. Chem. Soc.*, 1935, **57**, 1631.

the interior will be proportional to the concentration on the surface. The rate of diffusion across an area  $a$  is given by the equation

$$\left(\frac{\partial S}{\partial t}\right)_{x=0} = aC_0 \sqrt{\frac{1}{\pi t}}$$

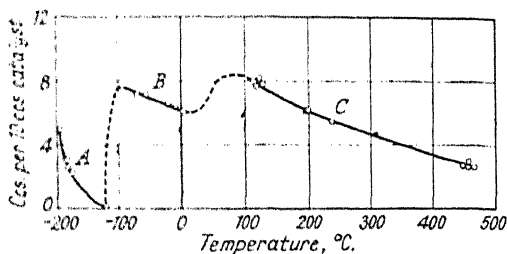


FIG. 35. Isotherm for hydrogen on iron at 760 mm. pressure.

[Emmett and Harkness.

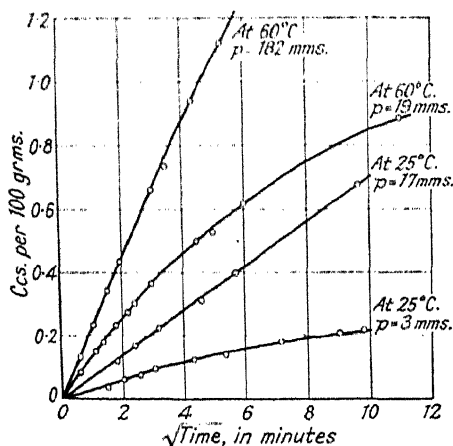


FIG. 36.—Rate of sorption of hydrogen by copper.

[Ward.

shown in Fig. 36. The points lie on substantially straight lines, and confirm his hypothesis. The same result would, however, be expected for an activated adsorption, and the  $\sqrt{t}$  law is generally found to hold good experimentally. In Fig. 37 the

where  $C_0$  is the concentration in solution and  $\Delta$  is the diffusion coefficient. The amount of gas in solution,  $S$ , at any time is therefore

$$S = 2aC_0\sqrt{\Delta t/\pi}.$$

For a given temperature and surface concentration,  $S$  will be proportional to the square root of the time. Ward therefore plotted the sorptions against  $\sqrt{t}$ , as

amount of hydrogen adsorbed by nickel is plotted against the time, and in Fig. 38 the adsorptions at  $-87^{\circ}\text{C.}$  and  $-96.5^{\circ}\text{C.}$  are plotted against  $\sqrt{t}$ . At higher temperatures the increased rate makes accurate measurements difficult. Maxted and Moon's<sup>1</sup> values given in Table 4 (p. 44) for activated adsorption of ethylene on platinum at  $20^{\circ}\text{C.}$  also confirm the  $\sqrt{t}$  law.

Total adsorption may therefore be attributed to physical adsorption, activated adsorption and solution, although the latter is only of importance at temperatures approaching the maximum at which adsorption measurements can be made.

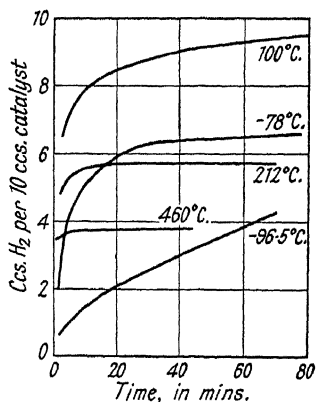


FIG. 37.—Rate of adsorption of hydrogen on nickel at 760 mm. pressure.

[Emmett and Harkness.

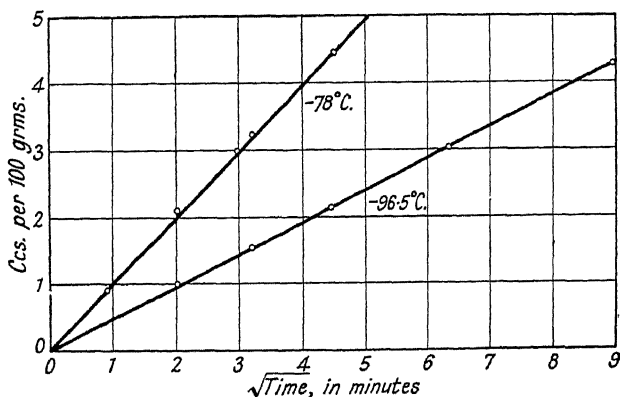


FIG. 38.—Rate of adsorption of hydrogen on nickel at 760 mm. pressure.

[Emmett and Harkness.

<sup>1</sup> Maxted and Moon, *Trans. Faraday Soc.*, 1936, **32**, 1375.



TABLE 4.

ADSORPTION OF ETHYLENE BY PLATINUM AT 20° C.

Time $t$ in mins.	c.c./100 grams.	$x/\sqrt{t}$ .
3	15	8.7
8	25	8.8
28	45	8.5
58	65	8.5
178	115	8.6
645	205	8.1
1318	315	8.6

**Heat of Adsorption.**

When a gas molecule is condensed on a metal surface heat is given up. This is the heat of adsorption,  $Q$ . When the molecule evaporates heat has to be supplied. This is the heat of evaporation, or desorption. In the case of physical adsorption, which is completely reversible and practically instantaneous, the heat of evaporation will generally be equal to  $-Q$ . Under these conditions the value of  $Q$  can be determined by calculation from the isotherms. If the pressure required to produce a definite adsorption of, say, 1 c.c., is determined at different temperatures, a series of curves called isosteres is obtained, which are similar to the vapour pressure curves of a solution. The Clausius-Clapeyron equation for the temperature coefficient of vapour pressure can be applied in the form

$$\frac{d(\log p)}{dT} = \frac{Q}{RT^2}, \quad . \quad . \quad . \quad (9)$$

where  $p$  is the pressure and  $Q$  is the heat of evaporation. It is only applicable to conditions where equilibrium has been attained. On integrating we obtain the equation

$$Q = 2.303 R \cdot \frac{T_1 T_2}{T_2 - T_1} \cdot \log \frac{p_2}{p_1} \quad (10)$$

where  $p_1$  and  $p_2$  are the equilibrium values at temperatures

$T_1$  and  $T_2$  for a constant value of adsorption,  $R$  is the gas constant having a value of 1.99 calories, and 2.303 is the factor for conversion to naperian logarithms.

Processes of activated adsorption, which are reversible in the sense that the gas is recovered in its original form on desorption, can be treated in the same way. In many cases there is reason to suppose, as we have seen, that the molecule is dissociated on adsorption. The total heat is then the algebraic sum of the heat of dissociation,  $Q_1$  (a negative quantity), and the heat of adsorption of the atoms,  $Q_2$  (a positive quantity), so that

$$Q = Q_1 + Q_2.$$

The value of  $Q_1$  is generally known and, for example, for hydrogen is equal to  $-100,000$  calories. There is, of course, a greater uncertainty as to whether any particular state represents equilibrium in cases of activated adsorption, owing to the slow character of the process and the fact that it is often not reversible with respect to changes in temperature and pressure. The agreement between the values determined directly by calorimeter and those obtained by calculation is generally satisfactory. For example, Ward found by direct measurement values for the heat of adsorption of hydrogen on copper varying between 9,000 and 14,000 calories for different samples, whilst Beebe obtained values between 11,500 and 13,300 calories by calculation from equation (10). Again, Beebe and Taylor measured the heat of adsorption of hydrogen on nickel, obtaining values between 12,600 and 14,600 calories, whilst the value calculated from Gauger and Taylor's isotherms is 13,000 calories.

The activation energy of the adsorption process may be calculated by means of the Arrhenius equation

$$\frac{d(\log k)}{dT} = - \frac{E}{RT^2} \quad (11)$$

where  $k$  is the reaction velocity constant and  $E$  the energy of activation. This simple equation can only be applied in cases where the kinetics of the adsorption process may be deduced.

As Taylor has pointed out, the activation energy of a heterogeneous reaction at a catalytic surface is probably a composite quantity, and the heats of adsorption of the reaction products must be taken into consideration in deducing the true energy of the process.

The activation energy of a simple reversible adsorption like hydrogen on a metal, may be calculated in the following way. The rate of condensation is given by  $k_1 p(1 - \theta)$ , and the rate of evaporation by  $k_2 \theta$ .

Therefore the rate of adsorption is

$$-\frac{dp}{dt} = k_1 p(1 - \theta) - k_2 \theta.$$

If  $\theta$  is small this becomes

$$-\frac{dp}{dt} = k_1 p - k_2 \theta$$

and

$$\frac{dp}{dt} = k(p - p_e),$$

where  $p_e$  is the equilibrium pressure and  $k$  is the velocity constant. By drawing tangents to the isothermal curves of  $\log(p - p_e)$  against time at points of equal adsorption, the velocities at two different temperatures may be determined, and the activation energy is given by Arrhenius' equation in the form

$$E = 2.303R \frac{T_1 T_2}{T_2 - T_1} \log \frac{\tan \alpha_{T_1}}{\tan \alpha_{T_2}} \quad (12)$$

This gives the activation energy at any moment in the adsorption process.

The average velocity of adsorption is obviously inversely proportional to the time taken to adsorb a given amount of gas, and the average activation energy may be calculated by substituting in the equation

$$E = 2.303 R \cdot \frac{T_1 T_2}{T_1} \cdot \log \frac{t_1}{t_2} \quad (13)$$

where  $t_1$  and  $t_2$  are the times taken for the adsorption of a given amount of gas at temperatures  $T_1$  and  $T_2$ .

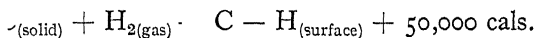
It might reasonably be assumed that the activation energy is associated with the separation of the atoms composing the molecule. Pace and Taylor<sup>1</sup> have found, however, that the value of  $E$  is the same for both hydrogen and deuterium on nickel, and they therefore conclude that the activation is mainly associated with the surface.

If the gas can be desorbed the activation energy of the desorption process,  $E_2$ , is given by  $(E_1 + Q)$ , where  $E_1$  is the activation energy of the adsorption process and  $Q$  is the heat of adsorption. Therefore in cases where the velocity of both adsorption and desorption can be measured, the heat of adsorption can be calculated. Benton and Drake<sup>2</sup> found by this method a value for the heat of adsorption of oxygen on silver of 15,700 cal./mol. which agreed well with the value of 16,000 calculated from the isosteres by the Clapeyron equation.

When the adsorption process is definitely irreversible, as, for example, in the adsorption of oxygen by tungsten, where on desorption the oxygen comes off as  $WO_3$ , the value of  $Q$  cannot be calculated. The energy of activation, which is simply the rate determining factor, can, however, be obtained in the same way as for a reversible process.

The heats of adsorption, determined either by direct measurement or by calculation, for a number of gas-metal systems at ordinary temperatures are given in Table 5 (p. 48).

It will be seen that the values vary from about 5000 to over 100,000 cal./gram. mol., and are in all cases of a much higher order than the heats of physical adsorption given in Table 1. These large heats support the view that in many cases the gas is dissociated. The value of the heat of adsorption is an indication of the stability of the adsorption complex. For instance, we have in the case of adsorption of hydrogen by carbon,<sup>3</sup>



Now the dissociation of the hydrogen molecule requires

<sup>1</sup> Pace and Taylor, *J. Chem. Phys.*, 1934, **2**, 578.

<sup>2</sup> Benton and Drake, *J. Amer. Chem. Soc.*, 1934, **56**, 255.

<sup>3</sup> Barrer, *Proc. Roy. Soc.*, 1935, **149**, 253.

TABLE 5.  
HEATS OF ACTIVATED ADSORPTION.

Metal.	Gas.	Temperature, °C.	Heat of Adsorption, Calories per gram. mol.	Refer- ence.
Copper	Hydrogen	25	9,000-14,000	1
			4,000-16,000	2
			11,500-17,500	3
			11,500-13,500	4
	Carbon monoxide	0	9,000-30,000	4
			13,000-20,000	5
13,500-20,300			6	
Nickel	Hydrogen	0	14,000	7
			10,000-30,000	8
			12,500	9
Platinum	Oxygen		100,000	7
	Hydrogen	20	14,000-17,200	10
		0	10,000-30,000	11
	Oxygen	0	33,000-161,000	11
	Carbon monoxide	0	18,000-35,000	11
	Sulphur dioxide	0	15,000-37,000	11
Silver	Oxygen	100	12,000-15,000	13
		197	15,000-23,000	12
Tungsten	Hydrogen		18,000-28,000	14
	Oxygen		320,000	15
			139,000	16
Palladium	Carbon monoxide	0 to 18.4	7,000-15,000	17
Iron	Hydrogen	- 96 to - 78	10,400 + 1000	18

<sup>1</sup> Ward, *Proc. Roy. Soc.*, 1931, 133, 506.

<sup>2</sup> Taylor, Kistiakowsky and Perry, *J. Phys. Chem.*, 1930, 34, 799.

<sup>3</sup> Taylor, Flosdorf and Kistiakowsky, *J. Amer. Chem. Soc.*, 1927, 49, 2200.

<sup>4</sup> Beebe, *Trans. Faraday Soc.*, 1932, 28, 761.

<sup>5</sup> Benton and White, *J. Amer. Chem. Soc.*, 1932, 54, 1373.

<sup>6</sup> Beebe and Wildner, *ibid.*, 1934, 56, 642.

<sup>7</sup> Taylor, "Physical Chemistry," 2nd ed., vol. 2.

<sup>8</sup> Fryling, *J. Phys. Chem.*, 1926, 30, 818.

<sup>9</sup> Rideal, *J. Chem. Soc.*, 1922, 121, 309.

<sup>10</sup> Maxted and Hassid, *ibid.*, 1931, 3313.

<sup>11</sup> Taylor and Kistiakowsky, *Z. Phys. Chem.*, 1927, 125, 341.

<sup>12</sup> Benton and Drake, *J. Amer. Chem. Soc.*, 1934, 56, 255.

<sup>13</sup> *Ibid.*, 1932, 54, 2186.

<sup>14</sup> Roberts, *Proc. Roy. Soc.*, 1935, 152, 445.

<sup>15</sup> Blodgett and Langmuir, *Phys. Rev.*, 1932, 40, 78.

<sup>16</sup> Roberts, *Proc. Roy. Soc.*, 1935, 152, 464.

<sup>17</sup> Taylor and McKinney, *J. Amer. Chem. Soc.*, 1931, 53, 3604.

<sup>18</sup> Emmett and Harkness, *ibid.*, 1935, 57, 1631.

100,000 calories, and hence the value of the C—H bond must be at least 75,000 calories. The conversion of ortho to para-hydrogen at the surface of platinum at 500° C., or tungsten at higher temperatures, is most readily explained<sup>1</sup> on the assumption that the molecules are dissociated, followed by recombination of atoms with appropriate spin. Physical adsorption on these surfaces at lower temperatures does not accelerate the conversion. On the other hand, it is probable that CO is actively adsorbed on metal surfaces without dissociation, and we cannot assume that dissociation is necessary for activated adsorption to take place.

It is clear from the experimental evidence we have just considered that we are dealing with adsorption of a very different kind from simple physical adsorption. At low temperatures gases are adsorbed as molecules, held only by weak van der Waals' forces. At ordinary temperatures gases are in most cases held by much stronger forces, and we may reasonably assume that the gas is then dissociated and the atoms linked directly to the metal atoms in the surface. The terms Chemisorption and Activated Adsorption have been used to describe processes of this type. There is undoubtedly considerable confusion about the meaning to be attached to these terms. By some they are treated as being synonymous, whilst others regard them as descriptive of different processes. Taylor uses the term activation energy in the sense of the activation energy of a chemical reaction, and it is therefore difficult to see how it is to be distinguished from chemisorption. Roberts, on the other hand, considers that when adsorption involving dissociation is practically instantaneous it cannot involve an activation energy, and is therefore to be distinguished as chemisorption, activated adsorption being reserved solely for slow processes. To quote Garner and Veal,<sup>2</sup> "The use of the term 'activated' for the second type of adsorption is open to criticism. If its only distinctive feature is that it possesses an activation energy, then the older term 'chemisorption' is to be preferred. If, on the other

<sup>1</sup> Bonhoeffer and Farcas, *Trans. Faraday Soc.*, 1932, 28, 242.

<sup>2</sup> Garner and Veal, *J. Chem. Soc.*, 1935, 1487.

hand, there is a fundamental difference between it and chemisorption, then the term activated adsorption is still unsatisfactory since it does not indicate what is the essential difference between the two types." There appears to be no more essential difference between these two processes than is found amongst ordinary chemical reactions. For example, a freshly cut surface of sodium exposed to a low pressure of oxygen becomes covered with an adsorbed film. It is not possible by evacuation to remove the oxygen so adsorbed—that is, it is irreversible with respect to pressure. Nor is the oxygen driven off by raising the temperature, except to such a degree that sodium oxide would be thermally dissociated. The film of oxygen adsorbed on a clean tungsten surface is also not removed by evacuation at room temperature, but when it is heated to  $1200^{\circ}\text{C}$ . the oxygen comes off as  $\text{WO}_3$ , and not as oxygen molecules. Similarly, oxygen adsorbed by carbon can only be recovered as  $\text{CO}$ . These are clearly cases of chemisorption. We may next take the case of  $\text{CO}$  adsorbed on palladium. Here we have very strong adsorption at  $100^{\circ}\text{C}$ ., which is not perfectly reversible with regard to pressure changes, as seen in Fig. 31, but at  $0^{\circ}\text{C}$ . the curves for sorption and desorption more nearly coincide. The gas in this case is recovered as  $\text{CO}$ . Again we find with hydrogen on nickel, that whilst desorption does not occur on lowering the temperature, the gas is completely recovered by evacuation, and the process is quite reversible with respect to pressure. Although a definite compound  $\text{NiH}^1$  has been shown to exist it is readily dissociated. These are typical examples of adsorption involving an energy of activation, and may be described as activated adsorption.

It seems clear, however, that no definite distinction can be drawn between chemisorption and activated adsorption, and certainly the criterion of reversibility cannot be applied to discriminate. It is less confusing to include all these examples in the term activated adsorption, and to recognise that the rate of adsorption and the stability of the product will vary in different cases, just as they do in ordinary chemical reactions.

<sup>1</sup> Gaydon and Pearse, *Nature*, 1934, 134, 287.

## The Specific Surface.

The experimental results so far considered refer almost entirely to adsorptions per unit mass of adsorbent. Since adsorption is a surface phenomenon it is of particular interest to know the adsorption per unit area of surface. Since no surface is perfectly smooth, the actual or specific surface must always be greater than the measured surface. Various methods, chemical, physical, optical and electrical, have been used to assess the area of the surface on which adsorption is taking place. This is particularly difficult in the case of metal powders, and no single method is entirely reliable.

Estimates of the surface of metal powders can be made from measurements of particle size. The particle diameters are difficult to determine directly, since they are frequently below the limit of resolution using ordinary light, namely  $10^{-4}$  to  $10^{-5}$  cm., and the finer particles, which contribute most to the surface, are liable to be neglected. Ward<sup>1</sup> has made an approximate calculation for the adsorption of hydrogen by copper powder. The surface calculated from the particle size was  $6 \times 10^4$  cm.<sup>2</sup> per 100 grams of copper, and the maximum adsorption at 25° C. was 1.2 c.c. Assuming one molecule of gas to be adsorbed on each unit space of the lattice, with  $a = 3.6 \times 10^{-8}$  cm., the area covered would be  $4.2 \times 10^4$  cm.<sup>2</sup> This is somewhat less than a complete molecular layer, even without allowing for any irregularity in the surface of the particles. Frankenburger and Hodler<sup>2</sup> found by a similar calculation in the case of ammonia on tungsten powder at 20° C. that 80 per cent. of the area was covered at 500 mm. pressure, when saturation had not yet been reached.

Methods of measuring particle size which are in general use for other purposes do not, as a rule, disclose anything about the shape of the particles, and are not therefore applicable.

The rate of solution in a reagent, compared to that of a solid whose surface can be measured, has been used by a number of workers.<sup>3</sup> This method is open to objection because

<sup>1</sup> Ward, *Proc. Roy. Soc.*, 1931, 133, 506.

<sup>2</sup> Frankenburger and Hodler, *Trans. Faraday Soc.*, 1932, 28, 229.

<sup>3</sup> Schmidt, *Z. phys. Chem.*, 1925, 118, 236; Schwab and Rudolf, *ibid.*, 1931, 12, 427.



of lack of uniformity in the rate of solution. Crittenden<sup>1</sup> has estimated the particle size from X-ray diffraction patterns, and Paneth<sup>2</sup> and others have taken the adsorptive power for dyes as a criterion of the surface area. These methods are very limited in scope.

Evidence from other sources that saturation corresponds to the completion of a molecular layer on the available surface is so strong, that so far as metal powders are concerned it is more usual to deduce the surface area from the amount of gas adsorbed, than to attempt direct measurement. The fact that adsorption isotherms usually become horizontal at high pressures and that the total quantity adsorbed is much the same for different gases in physical adsorption, strongly suggests the completion of a definite layer.

Indirect evidence leads to the same conclusion, as, for example, the fact that catalytic poisons prevent the adsorption of reactants when present in an amount not exceeding that required to give a mono-molecular film.

Metal powders are liable to undergo sintering when heated above the temperature at which the reduction has been carried out. Sintering has been shown<sup>3</sup> to be due to the growth of individual crystals of the metal, which gradually absorb each other to form larger aggregates, with a consequent reduction in the surface. Grain growth under these conditions takes place at a temperature several hundred degrees lower than the normal temperature of recrystallisation in compact metal. The action of "promoters," that is, certain inert oxides, such as alumina, ferrous oxide or silica, which are added to reduced metal catalysts, has been shown to be due to their effect in preventing sintering. These additions offer resistance to grain growth just as thoria added to tungsten prevents any change in structure in a lamp filament.

The determination of specific surface is somewhat easier in the case of metal wire or foil. As would be expected, the specific surfaces of polished metals approach most nearly to

<sup>1</sup> Crittenden, *J. Amer. Chem. Soc.*, 1925, 47, 2866.

<sup>2</sup> Paneth and Radu, *Berichte*, 1924, 57, 1221.

<sup>3</sup> Smithells, Pitkin and Avery, *J. Inst. Met.*, 1928, 38, 85.

the measured areas. The available surface is increased by roughening the surface, and by flaws, scratches, and cracks. Langmuir<sup>1</sup> found that methane, carbon monoxide and nitrogen formed 0.1 to 0.8 of a complete molecular layer on glass and mica, whilst the amount of oxygen and carbon monoxide adsorbed by platinum corresponded to about 0.6. Roberts<sup>2</sup> found a roughness factor of 1.1 for a tungsten wire that had been flashed at 2300° C., from the amount of hydrogen adsorbed at - 194° C. This may be compared with a value of 1.4 found by Taylor and Langmuir<sup>3</sup> for the adsorption of Cs on a similar wire.

Bowden and Rideal<sup>4</sup> measured the quantity of electricity,  $\Delta Q$ , which must be passed to cause a given change in the electrode potential of a cathode immersed in a dilute acid, and assumed that this was proportional to the accessible area. Measurements of this kind show the effect of various surface treatments, and some data for nickel sheet are given in Table 6.

TABLE 6.

Treatment.	Specific Surface
Rolled . . . . .	3.5
Rolled and annealed . . . . .	7.7
Sandpapered . . . . .	9.7
Activated . . . . .	46

Similar results obtained by Bowden and Connor<sup>5</sup> for Wood's metal are given in Table 7, in which  $\Delta Q$  for mercury is taken as unity.

TABLE 7.

Material.	$\Delta Q$ .	Catalytic Activity/ $\Delta Q$ .
Liquid . . . . .	1.0	—
Solid . . . . .	1.4	$9 \times 10^{-6}$
Sandpapered . . . . .	6.3	$5 \times 10^{-6}$
Etched with $\text{HNO}_3$	1000	$17 \times 10^{-6}$

<sup>1</sup> Langmuir, *J. Amer. Chem. Soc.*, 1918, 40, 1361.

<sup>2</sup> Roberts, *Proc. Roy. Soc.*, 1935, 152, 445.

<sup>3</sup> Taylor and Langmuir, *Phys. Rev.*, 1933, 44, 423.

<sup>4</sup> Bowden and Rideal, *Proc. Roy. Soc.*, 1928, 120, 63.

<sup>5</sup> Bowden and Connor, *ibid.*, 1930, 128 317.

As an average figure rolled sheet may be taken as having a specific area about twice the measured area. Roughening with emery or sandpaper increases the area by about 6 times. The coarseness of the emery appears to be immaterial.<sup>1</sup> Activation by alternate oxidation and reduction, which produces a spongy surface, by electrodeposition, or by etching may increase the area 1000 times. The fact that catalytic activity is proportional to  $\Delta Q$ , as shown in Table 7, suggests that this method of estimation is reliable.

The variation in the specific surface of metals as the result of different treatments is of great practical importance in the manufacture of thermionic valves. Whilst evacuation is being carried out large quantities of  $\text{CO}_2$  and other gases are liberated from the glass bulb, cathode, etc., which may be readsorbed by other electrodes. Although the total pressure is prevented from rising above about  $10^{-2}$  mm. of mercury the amount of gas adsorbed may be considerable. In Table 8 the amount of  $\text{CO}_2$  adsorbed by a nickel anode in this way is shown as a fraction of a molecular layer on the measured area.<sup>2</sup> A variation of 400 to 1 is shown, and since this gas may subsequently be liberated in the valve the importance of the surface treatment of such electrodes is obvious. Burdon<sup>3</sup> studied the adsorption of  $\text{CO}_2$  on a mercury surface freshly formed in the gas by admitting the mercury to the adsorption bulb from a reservoir. The vessel was then evacuated to a pressure of  $10^{-4}$  mm., and the surface destroyed by running the mercury out. This resulted in an evolution of  $\text{CO}_2$  which caused a rise in pressure corresponding exactly to a mono-molecular layer on the measured surface. Similar results were also obtained with hydrogen, showing that a mono-molecular layer was adsorbed which was not removed on evacuation.

Cassel<sup>4</sup> found a definite break in the curve for adsorption of carbon tetrachloride vapour on liquid mercury, corresponding

<sup>1</sup> Erbacher, *Naturwiss.*, 1932, 20, 944; *Z. Phys. Chem.*, 1933, 163, 215.

<sup>2</sup> Private communication by Dr. D. A. Wright, Res. Labs., G.E.C. Ltd., Wembley.

<sup>3</sup> Burdon, *Proc. Phys. Soc.*, 1935, 47, 460.

<sup>4</sup> Cassel, *Trans. Faraday Soc.*, 1932, 28, 177.

to a mono-molecular layer, although a layer three molecules thick could be formed at higher pressures. The formation of more than one molecular layer of a single gas may occur under conditions where the gas is nearly condensing, but is not usual at low pressures or high temperatures. As we have seen, however, there is very strong evidence that a molecular layer may be adsorbed on a surface already covered by activated adsorption with a monatomic film.

TABLE 8.

CO<sub>2</sub> ADSORBED BY NICKEL SHEET AFTER DIFFERENT TREATMENTS.

Treatment.	Fraction of Measured Surface Covered.
$\frac{1}{4}$ hour in vacuum at 1000° C. .	0.0025
8 hours in vacuum at 1000° C. .	0.005
8 hours in moist H <sub>2</sub> at 1000° C. .	0.1
Activated (oxidation and reduction)	1.0
Activated and exposed for 1 week	10.0 ✓

Benton and White noticed that the experimental points on the  $-183^{\circ}$  C. isotherm for CO on copper deviated by more than the experimental error from the smooth curve. They suggested that this was due to the completion of successive layers, and if so the jumps in the curves indicate the presence of 4 or 5 molecular layers. There seems to be no evidence that this occurs at temperatures well above the boiling-point of the gas. Benton and Drake also concluded that the isotherm for oxygen on silver at  $-183^{\circ}$  C. corresponds to several layers. At high temperatures the isotherms become definitely independent of pressure, but at  $-183^{\circ}$  C. the curve is convex to the pressure axis, as seen in Fig. 32. There is an indication of a limiting value at 100 mm. when adsorption has about the same value as the saturated adsorption at  $188^{\circ}$  C. They consider that whenever an isotherm has this form it indicates the formation of successive layers.

### Roberts' Theory.

Roberts<sup>1</sup> has studied adsorption by an entirely different method and arrived at conclusions which, if substantiated, may alter radically the picture of adsorption which has just been presented. He has studied the adsorption of hydrogen and oxygen on the surface of a tungsten filament, using the accommodation coefficient for neon as a measure of adsorption. The accommodation coefficient represents the efficiency of energy exchange between a gas and a metal surface. It has been shown that if the temperature of a gas molecule is represented by  $T_1$  and the temperature of the surface by  $T_2$ , then the change in temperature on striking the surface is proportional to the difference in temperature between the gas and the metal, so that

$$T_2' - T_1 = a(T_2 - T_1),$$

where  $T_2'$  is the temperature of the gas leaving the surface. The accommodation coefficient  $a$  is affected by the presence of an adsorbed gas film,<sup>2</sup> and may be ten times that for a clean surface. Using this technique Roberts finds that a tungsten filament, previously cleaned by flashing at 2300° C. is immediately covered with a film of hydrogen when exposed to the gas, either at 25° C. or at -180° C. The heat of adsorption, measured directly by the change in resistance of the filament, was 45,000 cal./gram. mol. when the surface was bare and about 18,000 cal./gram. mol. when the surface was nearly covered. He concludes from these high values that even at -180° C. the gas is dissociated and adsorbed as atoms. Since the process is virtually instantaneous it cannot require an activation energy, and he particularly distinguishes between chemisorption and activated adsorption for this reason. The strong binding force is shown by the fact that even at 0° C. the surface is completely covered at a pressure of  $10^{-4}$  mm. The layer appears to be complete if the roughness factor is taken as 1.1, although this is a rather lower value than is generally found. The film becomes unstable at 400° C. and evaporates

<sup>1</sup> Roberts, *Proc. Roy. Soc.*, 1935, **152**, 445.

<sup>2</sup> Mann, *ibid.*, 1934, **146**, 776.

in one minute at 600° C. Roberts concludes that activated adsorption as usually measured is not on a bare surface, but on a surface already covered with a film of this kind. This involves the assumption that a tungsten filament behaves in the same way as the metal powders usually employed in adsorption measurements.

With oxygen<sup>1</sup> he found a similar chemisorbed layer at 20° C., stable up to 1700° C. (as found by Blodgett and Langmuir),<sup>2</sup> but also a second film which was unstable above 60° C. The first film was complete on the basis of one oxygen atom to each metal atom, and the heat of adsorption was 139,000 cal./gram. mol. The heat of adsorption for the second film was only 48,000 cal./gram. mol., and was equivalent to 0.23 of a complete molecular layer. This is explained in the following way. In the first film adsorption can only take place when there are two neighbouring vacant spaces. Towards the end of the process there will be some isolated spaces, and these must remain unfilled. By calculation these would amount to 0.17 of the surface, which is in fair agreement with the observed value, if it is assumed that the second layer is only formed on the spaces left in the first, where the adsorption forces will be strongest.

Finally Roberts<sup>3</sup> has studied the effect of admitting oxygen to a surface already covered with hydrogen. He finds that the oxygen is adsorbed, but for each molecule adsorbed a molecule of hydrogen is driven off. This is a slow process, and resembles in every way the normal process of activated adsorption. It is suggested that herein may lie the explanation of activated adsorption, and if so it is clearly different from chemisorption.

It will be observed that Roberts' theory of adsorption depends on the assumption that an adsorbed atom cannot change its position on the surface, otherwise there would be no isolated spaces. It is therefore of interest to review the evidence regarding the possible migration of adsorbed atoms and molecules.

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Blodgett and Langmuir, *Phys. Rev.*, 1932, 40, 78.

<sup>3</sup> Roberts, *Proc. Roy. Soc.*, 1935, 152, 477.

## Surface Migration.

There is very good evidence that, under certain conditions, adsorbed molecules are capable of moving laterally over the surface on which they have been adsorbed. This evidence relates chiefly to metal atoms and molecules of organic compounds whose movements, for various reasons, are easier to follow, but we can by analogy draw certain conclusions as to the probable behaviour of adsorbed gas molecules. Volmer<sup>1</sup> has shown that when mercury atoms are condensed from the vapour on a suitably cooled surface the crystals which form grow nearly 1000 times as fast in some directions as in others. This can only be due to the migration of the condensed atoms over the surface of the growing crystal until they arrive at positions of maximum stability. Similar evidence has been obtained by Estermann<sup>2</sup> for cadmium condensed from the vapour, and by Adhikari<sup>3</sup> for the growth of crystals of benzophenone.

Becker<sup>4</sup> has shown that barium atoms can migrate in the same way over a tungsten surface. If barium vapour is condensed on the surface of a tungsten filament it is found that the thermionic emission gradually rises, and reaches a maximum value when the surface is completely covered with a monatomic layer of barium atoms. The fraction of the surface which is covered at any moment can therefore be determined by measuring the emission. Becker deposited a monatomic layer of barium atoms on one side of a tungsten strip, mounted as a filament in a thermionic valve, and so arranged that the emissions from each side of the strip could be measured separately. So long as the temperature of the strip was kept below 600° C. the emissions from the two sides corresponded to those for tungsten and barium-on-tungsten respectively. But on flashing the filament at 700° C. the emission from the bare tungsten side gradually rose, whilst that from the barium covered side fell, until they became equal. The emissions then had a value

<sup>1</sup> Volmer, *Trans. Faraday Soc.*, 1932, 28, 359.

<sup>2</sup> Estermann, *Z. Electrochem.*, 1925, 31, 441; *Z. Physik*, 1925, 33, 320.

<sup>3</sup> Adhikari, *Z. Physik*, 1925, 35, 170.

<sup>4</sup> Becker, *Trans. Faraday Soc.*, 1932, 28, 148.

corresponding to that for a surface having half the optimum covering of barium. Fig. 39 shows the type of curve obtained, in which the log of the emission is plotted against the time;  $i_2$  is the current from the uncoated side. When  $\theta = 0.8$  the temperature of the strip was raised and migration to the other side began. This is shown by the rapid rise in the emission from the uncoated side, with a corresponding fall in the emission from the coated side as it loses barium. It is clear that below  $600^\circ \text{C}$ . the barium remained practically stationary, but at higher temperatures migrated rapidly to the other side.

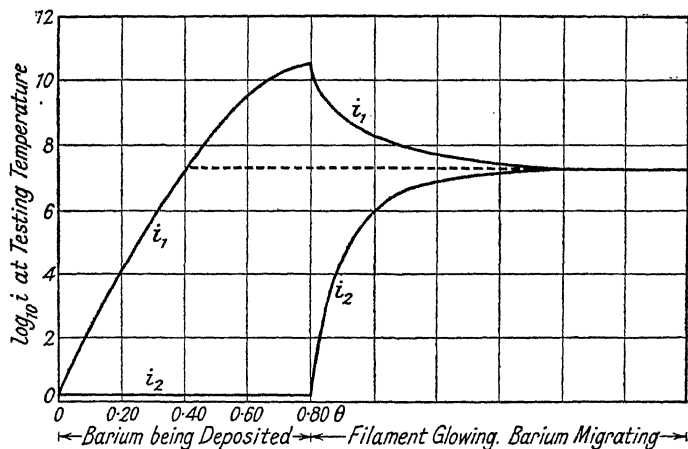


FIG. 39.—Thermionic emission from a tungsten strip coated on one side with barium.  $i_1$ —current from coated side,  $i_2$ —current from uncoated side.

[Becker.

Adsorbed caesium has been shown to migrate in the same way.<sup>1</sup>

The rate of oxidation of copper is independent of the pressure above a certain value, which varies from about 10 mm. for commercial foil to 150 mm. for an active copper catalyst. Wilkins<sup>2</sup> has shown that this can be satisfactorily explained on the assumption that oxidation only proceeds by

<sup>1</sup> Taylor and Langmuir, *Phys. Rev.*, 1933, 44, 423.

<sup>2</sup> Wilkins, *Proc. Roy. Soc.*, 1930, 128, 407.



penetration down the grain boundaries of the oxide crystals, and the concentration at these points is maintained by lateral diffusion of adsorbed oxygen molecules over the cuprous oxide surface.

The most probable explanation of surface migration is given by a simple extension of the kinetic theory. At very low temperatures the adsorbed molecules have a small amplitude of vibration around their mean positions. As the temperature is raised this amplitude increases, and the probability of it being sufficient to carry the molecule into the next unit space on the surface increases. At higher temperatures the molecules move over the surface relatively rapidly in a series of jumps from one unit space to the next. For such a jump to occur the molecule must surmount a potential barrier,<sup>1</sup> and this requires an activation energy, the value of which can be calculated.<sup>2</sup> In the case of oxygen on copper it appears to be about 12,000 cal. gram. mol. This is of the same order as is found for the heat of diffusion through the metal.

Lateral diffusion of this kind accounts for the importance of cracks, pores, scratches and possibly grain boundaries in contributing to the specific surface of a solid. For these places might well be protected from the direct impact of gas molecules. It accounts satisfactorily for the very large accessible areas of spongy and activated adsorbents. There is a strong presumption that this lateral mobility will decrease as the strength of adsorption becomes greater, and in the case of adsorbed ions the bond may well be so strong that the gas will remain at the point where it is condensed. So long as the adsorption process is correctly represented by the Langmuir concept and  $\theta$  determined by a balance between evaporation and condensation, the possibility of lateral diffusion cannot be excluded. When the process is irreversible and chemisorption takes place, the probability of lateral diffusion is much smaller.

<sup>1</sup> Lennard-Jones, *Trans. Faraday Soc.*, 1932, 28, 333. The problem of surface migration has been considered from the point of view of wave mechanics by Lennard-Jones and Strachan, *P. Roy. Soc.*, 1935, 150, 442.

<sup>2</sup> Rideal, *Trans. Faraday Soc.*, 1932, 28, 139.

## ADSORPTION

### Thermionic Evidence.

The application of thermionics has thrown some light on several phases of the problem of adsorption. Langmuir<sup>1</sup> in 1913 first studied the effect of adsorbed gases on the thermionic emission from a tungsten filament. It is now well established that thermionic emission is depressed when the surface of a metal is contaminated with an adsorbed film of electronegative atoms. This is due to their attraction for electrons, which results in the formation of an electric double layer with the negative charge on the outside, whereby the work function is increased. The greatest effect is found with oxygen. Kingdon<sup>2</sup> studied the adsorption of oxygen on tungsten by following its effect on the thermionic emission. If a tungsten filament is first cleaned by flashing at 2400° C. in a vacuum, and then exposed cold to oxygen at a pressure of .02 mm., and the excess oxygen pumped away, it remains covered with a complete monatomic film of oxygen. Reimann<sup>3</sup> has shown that the work function of such a surface is 1.7 volts higher than for a clean tungsten surface, and the value of  $\theta$  at any stage can therefore be determined from the emission.

These films are extraordinarily stable, and only evaporate slowly even at 1200° C. Since tungstic oxide,  $\text{WO}_3$ , evaporates rapidly in a vacuum below a red heat, it is clear that the oxygen is not present on the surface as  $\text{WO}_3$ , but is yet held by very strong adsorptive forces.

Just as negative ions can depress the emission, so positive ions enhance the emission from a metal. Surface layers of positive ions may be formed in several ways. A tungsten wire may be mounted as a filament in an evacuated bulb, and the surface thoroughly freed from adsorbed gas by flashing at a high temperature. If the vapour of metallic caesium is then introduced, and the filament run at about 400° C., caesium atoms striking the surface are adsorbed. A nickel filament may be covered with a layer of barium atoms in a similar manner, for example, by distilling barium from a nickel-barium alloy

<sup>1</sup> Langmuir, *Phys. Rev.*, 1913, 2, 450.

<sup>2</sup> Kingdon, *ibid.*, 1924, 24, 510.

<sup>3</sup> Reimann, *Phil. Mag.*, 1935, 20, 594.

in the form of a spiral surrounding the filament. An alternate method of covering the surface is by diffusion from the interior of the filament, to which the electropositive metal, or its oxide, has previously been added, as for example thorium oxide in tungsten. Similar results are obtained by all these methods. In Fig. 40 the logarithm of the electron emission,  $i$ , is plotted against the amount of adsorbed electropositive metal on the surface for a tungsten filament at  $800^{\circ}\text{C}$ . It will be seen that

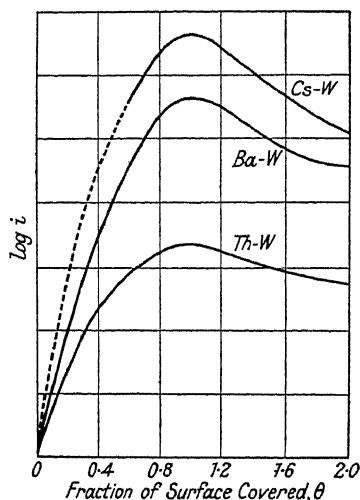


FIG. 40.—Thermionic emission curves for caesium, barium and thorium films on tungsten.

[Becker.

the curves are similar for caesium, barium and thorium on tungsten. The amount of adsorbed metal is represented as the fraction of the surface,  $\theta$ , covered with a monatomic layer of the metal, either in the form of atoms or ions. Since these films are stable in a vacuum at temperatures where the metal would normally evaporate, it is clear that this is not a case of physical adsorption, but that the adsorbed layer must be held by much stronger forces than residual valencies, probably by the sharing of electrons. The maximum in the emission curve is found to coincide roughly with the completion of a monatomic film, as seen in Fig. 40. It should be stated, however, that exact proof of this cannot be obtained without a knowledge of the roughness factor of the surface. If metal atoms in excess of a complete monatomic layer are allowed to condense, the emission gradually falls, and when more than three atomic layers are present the emission has the value for the metal in bulk.

The application of thermionics to the study of more complex films has proved very valuable. Barium or caesium atoms

may be deposited on a surface already covered with oxygen,<sup>1</sup> and by suitable thermal treatment the atoms may be made to change places to form surfaces such as O—Cs—W, on which a further layer of caesium atoms may be deposited. These surfaces all have their characteristic work functions, and the progress of adsorption can be followed from the emission.

### Photoelectric Methods.

Just as electrons are emitted by metals under the action of heat, so they may leave the surface when the necessary energy is supplied by light. Whether or not an electron will be emitted depends upon the work function of the surface and the wavelength of the incident light. For a given work function there is an upper limit of wave-length, and light of greater wave-length than this will not cause photoelectric emission. The long-wave photoelectric threshold and the total emission are affected by changes in the work function of the surface produced by the presence of adsorbed films. In general it is found that the presence of positive ions on the surface decreases the work function and causes a shift in the long-wave limit towards the red, whilst negative ions have the opposite effect. Suhrmann<sup>2</sup> has shown that hydrogen only affects the work function of platinum when present in the form of ions. He suggests that ionisation takes place within the surface layers of the metal, and that the ions diffuse to the surface. The question of ionisation of gases by metals has been discussed by Nyrop.<sup>3</sup>

The kind of information given by photoelectric methods may be illustrated by comparing Brewer's<sup>4</sup> observations on the effect of oxygen on silver with Benton and Drake's<sup>5</sup> adsorption measurements. Brewer finds :

(a) That at 0° C. the presence of oxygen slightly enhances the emission, the effect increasing with pressure up to about 1 mm., and being perfectly reversible.

<sup>1</sup> See Reimann, "Thermionic Emission," 1934, p. 159.

<sup>2</sup> Suhrmann, *Physik. Zeit.*, 1929, 30, 939.

<sup>3</sup> Nyrop, *Phys. Rev.*, 1932, 39, 967.

<sup>4</sup> Brewer, *J. Amer. Chem. Soc.*, 1934, 56, 1909.

<sup>5</sup> Benton and Drake, *ibid.*, 255.

(b) After heating in oxygen, and then heating to  $200^{\circ}\text{C}$ . in vacuo a very high emission is obtained, and the long-wave limit shifts from  $2610\text{ \AA}$ . to  $3150\text{ \AA}$ . The emission is only slowly destroyed by heating at  $600^{\circ}\text{C}$ . in vacuo.

(c) If a high-frequency discharge was passed through the gas the silver became covered with a brown film of  $\text{Ag}_2\text{O}$  and no emission could be obtained.

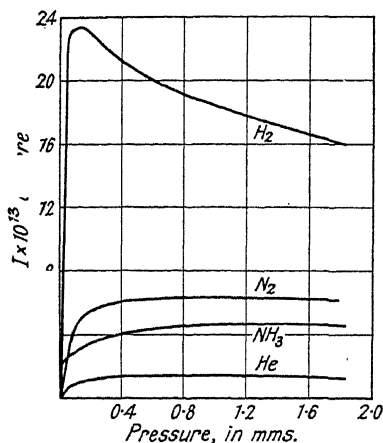


FIG. 41.—Effect of gases on photoelectric current  $I$ , from platinum at  $455^{\circ}\text{C}$ . for  $\lambda = 2300$  with accelerating potential of 9 volts.

[Brewer.]

photo-electric emission of iron and platinum. The change in work function for iron is shown by the following table :—

Surface.	$\phi$ in Electron Volts.
In vacuum	4.8
In $\text{H}_2$	4.5
In $\text{N}_2$	4.4
In $\text{NH}_3$	3.1
In $\text{O}_2$	> 5.4

The effect on the emission current from platinum for a wave-length of  $2300\text{ \AA}$ . is shown by the curves in Fig. 41, which

<sup>1</sup> Brewer, *J. Amer. Chem. Soc.*, 1932, 54, 1888.

bear a close resemblance to adsorption isotherms. By comparison with the known effect of potassium ions on the surface of these metals it may be concluded that the gases are, at least partially, ionised.

### Electron Diffraction Methods.

In 1927 G. P. Thomson <sup>1</sup> showed that electrons could be diffracted. By allowing a beam of relatively slow electrons—25 to 230 volts—to fall on a surface in a vacuum, a pattern similar to an X-ray pattern is obtained. The reflections, however, are due solely to the surface layers, and the patterns obtained are affected both by imperfections in the surface and by the presence of adsorbed films. This method of attacking surface problems is still in its infancy, but is likely to prove exceedingly valuable. The information that has been obtained regarding the surface structure of metals has been summarised by Thomson <sup>2</sup> in the following words :—

“ Evidence derived from experiments on electron diffraction leads to the following conclusions. In some cases the material near the cleaved or natural face of a single crystal is correctly aligned to 10 mins. or less. The surface, apart from steps, is sometimes smooth but sometimes carries narrow ridges less than  $10^{-6}$  cm. thick. In many cases, but not always, the surface is broken into small regions of the order of  $10^{-5}$  cm. These regions sometimes keep their parallel alignment, but probably not always. They are most likely to be distorted in the case of metals. Etching, as might be expected, leaves a surface of projections and ridges, many of which are not more than a small multiple of  $10^{-7}$  cm. thick. The degree of perfection of a crystal surface varies considerably from specimen to specimen and with the care with which it has been prepared.

“ A number of surfaces composed of poly-crystalline aggregates carry projections not more than about  $10^{-6}$  cm. thick covering an appreciable fraction of their surface. Such surfaces are formed when crystals are deposited by evaporation

<sup>1</sup> G. P. Thomson, *Nature*, 1927, 120, 802 ; *Proc. Roy. Soc.*, 1928, 117, 600 ; 119, 651.

<sup>2</sup> Thomson, *Phil. Mag.*, 1934, 18, 640.

or cathodic sputtering, and when chemical action, either in the form of etching or the formation of compounds, takes place at metallic surfaces. . . . Polishing of metals covers the surface with an amorphous layer ; this layer is not usually flat, being formed into ridges or waves over at least part of the surface."

The effect of adsorbed gases on the diffraction patterns, and their interpretation, has been studied by Davisson and Germer,<sup>1</sup> Rupp,<sup>2</sup> and Finch, Quarrell and Wilman.<sup>3</sup> Davisson and Germer obtained diffraction patterns from a single crystal of nickel on which hydrogen had been adsorbed, which

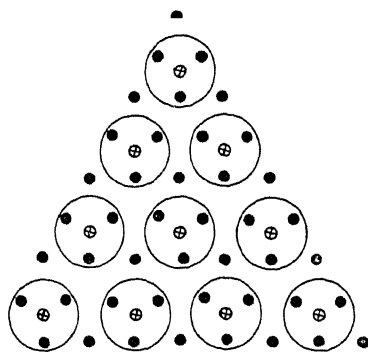


FIG. 42.—Arrangement of hydrogen atoms adsorbed on a nickel surface.

⊗ hydrogen atoms.

● nickel atoms.

[Davisson and Germer.]

indicated that the hydrogen molecules formed a lattice similar to that of the underlying nickel, but with twice the atomic spacing. The arrangement is shown in Fig. 42, the dotted circles indicating that the gas molecules cover about 3 nickel atoms. By heating to 100° C. the adsorbed gas is driven off, and the normal nickel pattern is then obtained.

Various workers have from time to time observed the presence of extra or "forbidden" rings in the diffraction patterns obtained from metal surfaces, the presence of which could not be explained. In a recent study of electrodeposited films Finch and his co-workers have found these extra rings very well developed, and have by suitable treatment been able to develop them to the exclusion of the normal pattern. They are shown to be due to the entry of gas into the actual lattice of the metal, forming a solid solution in the surface layers.

<sup>1</sup> Davisson and Germer, *Phys. Rev.*, 1927, 30, 705.

<sup>2</sup> Rupp, *Annalen d. Physik*, 1930, 5, 453.

<sup>3</sup> Finch, Quarrell and Wilman, *Trans. Faraday Soc.*, 1935, 31, 1051.

By heating gold foil in air for 20 minutes at 300° C. a pattern of extra rings corresponding to a close-packed hexagonal structure was obtained. On heating again in vacuo the normal pattern was recovered. Similar experiments with aluminium, chromium and silver heated in air or oxygen also gave rise to extra rings. It appears that when oxygen enters a face-centred cubic lattice, the oxygen occupies a body-centred position, and in a body-centred lattice the face-centred position is occupied. It is to be expected that electron diffraction methods will, in the future, help still further in the elucidation of gas-metal problems.

### Adsorption of Two Gases.

So far we have considered chiefly the adsorption of a single gas. The effect of one gas on the adsorption of another, although of great practical importance, has been less thoroughly investigated. Fowler<sup>1</sup> has discussed the theoretical form of the adsorption isotherms in the case of competing molecules. For physical adsorption these have the form

$$\theta_1 = \frac{A_1 p_1}{1 + A_1 p_1 + A_2 p_2}, \quad \theta_2 = \frac{A_2 p_2}{1 + A_1 p_1 + A_2 p_2},$$

where  $\theta_1$ ,  $p_1$  and  $\theta_2$ ,  $p_2$  refer to the two gases respectively. These equations are not applicable to activated adsorption. The presence of a second gas usually reduces the total amount of adsorption and equilibrium is reached more slowly. Gases vary very much in their strength of adsorption on the same metal, and a strongly adsorbed gas tends to displace a weakly adsorbed one. Roberts' experiments, which show that oxygen displaces hydrogen previously adsorbed on a tungsten surface, have already been discussed on page 57. Oxygen is adsorbed much more strongly than hydrogen on gold and silver<sup>2</sup> at room temperature, and in the presence of both gases the surface is almost entirely covered with oxygen. Carbon monoxide and nitrogen are adsorbed more strongly than hydrogen on most

<sup>1</sup> Fowler, *Proc. Camb. Phil. Soc.*, 1935, 31, 260.

<sup>2</sup> Benton and Elgin, *J. Amer. Chem. Soc.*, 1926, 48, 3027; 1927, 49, 2426.



metals, but they will not displace chlorine, which is adsorbed more strongly still. The adsorption of hydrogen and deuterium from mixtures of the two isotopes is an interesting example of competing gases. At  $-78^{\circ}$  C. the rate of adsorption of  $D_2$  on copper<sup>1</sup> is less than that of  $H_2$ , but at equilibrium equal amounts of the two gases are adsorbed. Between  $0^{\circ}$  and  $125^{\circ}$  C.  $D_2$  is more strongly adsorbed than  $H_2$ .

It may be possible in certain cases for one gas to be adsorbed on a surface already covered by another. It is certainly established that a monatomic layer of caesium or barium can be formed on a tungsten surface previously covered with oxygen, and the poisoning of thermionic emission is often due to an adsorbed layer of oxygen on top of the monatomic film of active metal.

The presence of two gases in contact with a metal surface often leads to catalytic action, that is, the promotion of a chemical reaction between the two gases which, in the absence of the metal surface, would either not take place, or take place much more slowly at the temperature in question. The metal surface, or catalyst, is not changed substantially by the reaction, and is not included in the products of the reaction. The subject of catalytic reactions at metal surfaces, though closely connected with adsorption, is beyond the scope of the present volume, and for a detailed account of the subject the reader is referred to the standard works.<sup>2</sup> Only a brief outline of the subject and its bearing on adsorption problems can be given here.

The action of catalysts in promoting chemical reaction between gases is undoubtedly related to their power of adsorbing one or both of the reactants. These reactions usually take place at or above room temperature, and it is therefore the chemical type of adsorption which is involved. As a rule one gas is much more strongly adsorbed than the other, and the

<sup>1</sup> Beebe, Low, Wildner and Goldwasser, *J. Amer. Chem. Soc.*, 1935, 57, 2527. For similar work with platinum see Maxted and Moon, *J. Chem. Soc.*, 1936, 1542.

<sup>2</sup> See for example, Rideal and Taylor, "Catalysis in Theory and Practice"; Taylor, "Physical Chemistry"; Glasstone, "Recent Advances in Physical Chemistry."

rate of reaction is then proportional to the pressure of the weakly adsorbed gas. Thus with copper at 0° C. ethylene is very strongly adsorbed as a mono-molecular layer, independently of the pressure.<sup>1</sup> Hydrogen is only weakly adsorbed, and the hydrogenation of ethylene to form ethane is proportional to the hydrogen pressure only. It thus appears to be a uni-molecular reaction. But at 250° C. neither gas is strongly adsorbed, and the rate of reaction is proportional to the pressure of each gas, and now appears as a bimolecular reaction.

Langmuir<sup>2</sup> found a similar result for the combination of hydrogen and oxygen on platinum. Below 300° C. oxygen is preferentially adsorbed, and the pressure of hydrogen controls the rate of reaction. Between 400° and 1600° C. both gases are equally adsorbed, and the rate depends on the pressure of the gas which is present in smallest quantity. A similar result is found in the oxidation of carbon monoxide on platinum, carbon monoxide being preferentially adsorbed at temperatures below 500° C. These results may be explained by assuming that gas molecules react with one another when they are adsorbed on adjacent spaces on the metal surface. Various hypotheses have been propounded as to why they should be more reactive in this state. Possibly the molecules come into closer contact in this way, or the individual molecules may be dissociated. It is known that atoms of hydrogen evaporate from a hot filament in hydrogen,<sup>3</sup> and in many cases it is clear that the gas molecules are actually dissociated and held as atoms or ions. Whilst any of these pictures enables one to visualise the catalytic process it is not always possible to say which represents the actual fact.

Whilst adsorption is necessary for catalytic action, maximum adsorption does not necessarily coincide with maximum catalytic

<sup>1</sup> Pease, *J. Amer. Chem. Soc.*, 1923, 45, 1197.

<sup>2</sup> Langmuir, *ibid.*, 1918, 40, 1361.

<sup>3</sup> Bryce (*Proc. Camb. Phil. Soc.*, 1936, 32, 648) has shown that the rate of production of atoms,  $n$ , per cm.<sup>2</sup> per sec. is given by the equation

$$n = 2.5 \times 10^{24} \sqrt{p} \cdot e^{-\frac{45000}{RT}}$$

For a discussion of the mechanism of the reaction see Roberts and Bryce, *ibid.*, 653.

activity. Whilst the amount of adsorption *increases* with decrease in temperature, the rate of adsorption and the rate of chemical reaction both *decrease*. There is, therefore, an optimum temperature depending on these factors.

### Active Centres.

Ordinary adsorption measurements do not always disclose the efficiency of a catalyst, and there is good reason to believe that most catalytic reactions take place at certain "active centres," and not over the whole surface of the catalyst. This view is supported by a large number of facts.

Catalysts can be poisoned by adsorbing certain gases in quantities insufficient to cover more than a small fraction of the surface. As we have seen, the adsorption of one gas may be reduced by the presence of a second, more strongly adsorbed gas. But the catalytic activity is often reduced to a far greater extent than the adsorption. For example, finely divided copper will catalyse the hydrogen-ethylene reaction. A trace of mercury that will reduce the rate of reaction 200 times, only reduces the adsorption of ethylene by 14 per cent., and that of hydrogen by 80 per cent.<sup>1</sup> There must, therefore, be two kinds of adsorptive areas, on one of which mercury is adsorbed to the exclusion of hydrogen, whilst the ethylene continues to be adsorbed on the other, and the area occupied by the mercury must be the main seat of the catalytic action. Cyanogen, which is very strongly adsorbed,<sup>2</sup> behaves like mercury and reduces the hydrogen adsorption. Oxygen has a similar effect.<sup>3</sup> Sintering the copper catalyst reduces adsorption in the same way.

It is therefore concluded that whilst adsorption may take place over the whole surface, the catalytic reaction takes place mainly at certain active centres. If these centres are occupied by another strongly adsorbed gas—the poison—the reaction is suppressed, although the total adsorption may not be much reduced. Fig. 43 shows isotherms for the adsorption of hydrogen on finely divided copper at 0° C. in the presence of carbon

<sup>1</sup> Pease, *loc. cit.*

<sup>2</sup> Griffin, *J. Amer. Chem. Soc.*, 1934, 56, 845.

<sup>3</sup> Russell and Ghering, *ibid.*, 1935, 57, 2544.

monoxide and cyanogen, and also isotherms for these two gases separately. Whilst cyanogen reduces the adsorption at all pressures, carbon monoxide<sup>1</sup> produces a slight increase in adsorption at low pressures. Carbon monoxide affects the adsorption of hydrogen by nickel in the same way,<sup>2</sup> and its exceptional behaviour is probably due to the formation of a complex with the hydrogen. The amount of CO necessary to inhibit the reaction is much less than would be required to form a mono-molecular layer, and it is so strongly adsorbed that it cannot be completely pumped away at 200° C. It has recently been shown by Maxted<sup>3</sup> that a given amount of poison reduces the rate of a number of different reactions to the same extent, which indicates that only one kind of active centre exists.

Oxygen also seems to be adsorbed on nickel in two ways, since part of it can be removed by treatment with hydrogen at low temperatures,

whilst the remainder requires a high temperature reduction. The nature of these active centres is uncertain, but is probably connected with variations in residual valency of atoms at the surface of the catalyst. Any roughness or projections on the surface will provide atoms whose valencies are less satisfied by their neighbours. A similar state may exist at the edges of crystals and at grain boundaries.

Some evidence for the existence of active centres is obtained from measurements of the heat of adsorption. There is some doubt as to whether the differential heat of adsorption is

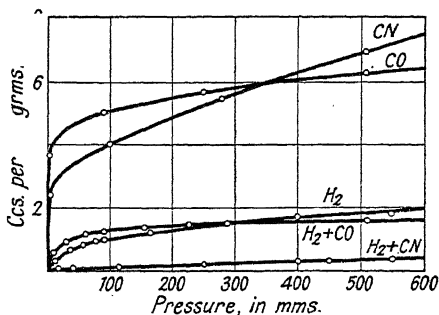


FIG. 43.—Poisoning effect of CO and cyanogen on adsorption of hydrogen on copper at 0° C.

[Griffin.

<sup>1</sup> Griffin, *J. Amer. Chem. Soc.*, 1927, 49, 2136.

<sup>2</sup> Benton and White, *J. Phys. Chem.*, 1931, 35, 1784.

<sup>3</sup> Maxted, *J. Chem. Soc.*, 1934, p. 26.

constant, or varies with the amount of gas already adsorbed. Values determined by calculation from the isosteres may not be reliable because adsorption is not always reversible and true equilibrium may not be attained. Direct determination of heats for small adsorptions are liable to experimental error. A constant value for the heat of adsorption has been found by Beebe and Taylor for hydrogen on nickel at 0° C. (14,000 cal./gm. mol.), and by Ward for hydrogen on copper at 25° C. (8,000 to 30,000 cal./gm. mol. with different samples of copper), and by Maxted and Hassid<sup>1</sup> for hydrogen on platinum. On the other hand, high initial values followed by a progressive fall in the heat of adsorption as the surface became covered have been found by other observers.<sup>2</sup>

It would be expected that higher heats would be associated with the more active parts of the surface on which adsorption would be most rapid. If this is so, the uniform heats found in the other case must be accounted for by surface migration, for then the measured heat would be the sum of the heats due to the evaporation and readsorption of all the molecules concerned in the time interval observed. In a few cases a low initial heat, followed by a maximum value which decreased with further adsorption, has been found,<sup>3</sup> but is not satisfactorily explained.

Since the activity of metal catalysts depends on the presence of active centres the method of preparation is of great importance. These catalysts are usually prepared by low temperature reduction of precipitated oxides or hydroxides. The temperature of reduction is determined to some extent by the temperature at which the catalyst is to be used, and it is usual to carry out the final reduction either at, or slightly above, that temperature, so that further sintering does not take place in use. It is generally found that activity is greater the smaller the particle size, and may be inhibited by sintering at a high

<sup>1</sup> Maxted and Hassid, *J. Chem. Soc.*, 1931, 3313; Maxted, *ibid.*, 1930, 2093.

<sup>2</sup> Beebe and Wildner, *J. Amer. Chem. Soc.*, 1934, 56, 642; Beebe, *J. Phys. Chem.*, 1926, 30, 1538; Fryling, *ibid.*, 1926, 30, 818; Roberts, *Proc. Roy. Soc.*, 1935, 152, 445.

<sup>3</sup> Kistiakowsky, Flosdorf and Taylor, *J. Amer. Chem. Soc.*, 1927, 49, 2200.

temperature. Metal in the solid form, such as sheet, is relatively inactive. All these facts are consistent with the assumption that the maximum activity is associated with the edges of the crystals, and is not solely dependent on the surface area of the catalysts. It has been suggested that catalytic reactions should be sensitive to the arrangement and spacing of the atoms in the metal surface,<sup>1</sup> and some support for this hypothesis is provided by experiments of Long and others.<sup>2</sup> They have determined the efficiency of reduced copper, nickel, cobalt and iron, and binary alloys of these metals in the hydrogenation of benzene to form cyclohexane. They found that only powders having a face-centred cubic lattice were catalytically active for this particular reaction, and that when the structure was body-centred cubic they were inactive. Whilst this evidence alone is not conclusive the results indicate an interesting field for further investigation.

### Gettering.

No account of the adsorption of gases by metals would be complete without some reference to the process known as gettering. This expedient was devised in the early days of lamp manufacture to obtain a much higher vacuum in the finished lamp than could be produced by the exhaust pumps then available. The filament of the lamp was initially coated with some substance, for example phosphorus, which after the lamp was sealed off could be volatilised on to the walls of the bulb. The getter, in condensing, carried with it a considerable amount of the residual gas, and the film deposited on the bulb provided a surface upon which the remaining gas was adsorbed during a preliminary ageing period. Salts such as cryolite were employed as well as chemically-active substances like phosphorus and were capable of adsorbing large quantities of gas at pressures as low as  $10^{-4}$  mm. Getters used in lamps were obviously limited to substances that produced a transparent deposit on the bulb, but in thermionic

<sup>1</sup> Langmuir, *Trans. Faraday Soc.*, 1921, 17, 617.

<sup>2</sup> Long, Frazer and Ott, *J. Amer. Chem. Soc.*, 1934, 56, 1101.

valves, where transparency is not necessary, it is now customary to use metals almost exclusively as getters. Those most commonly used are magnesium, barium and their alloys. After the valve has been sealed off from the pump, the pressure being then about  $10^{-2}$  mm., the metal is distilled on to the inner surface of the bulb. We may refer to this coating as the getter surface.

Magnesium is generally used in the form of a small piece of ribbon welded to a suitable piece of nickel, which can be heated either by high-frequency current or by bombardment to a temperature sufficient to volatilise the metal. Barium may be used in a similar manner, in the form of wire protected from the atmosphere by a sheath of copper. An alternative method is to produce it by thermal decomposition of barium azide, applied as a paint to a nickel support. Ba-Mg and Ba-Mg-Al alloys are used in the form of small pellets made by compressing the powdered alloys. The getters themselves, owing to their reactive nature, usually contain a considerable amount of gas, and it is important that this should be removed by preliminary evacuation at a high temperature.

As the result of the gettering action the pressure may be reduced to  $10^{-7}$  mm., the irreversible nature of the process clearly indicating an activated adsorption. It may take place in three different ways :—

- (a) by the adsorption of the gas on the getter surface after dispersal ;
- (b) by adsorption during dispersal ;
- (c) under the action of an electrical discharge.

All the common gases  $N_2$ ,  $H_2$ , CO,  $CO_2$ , and water vapour, are cleaned up by barium at room temperature in all three ways.<sup>1</sup> Magnesium, which is less reactive, does not adsorb nitrogen, hydrogen only very slightly, except under the action of a discharge, whilst water vapour is decomposed by it giving hydrogen. The other gases are adsorbed, but less strongly than by barium. Under the influence of an ionising electrical discharge hydrogen is converted into atomic hydrogen,

<sup>1</sup> Reimann, *Phil. Mag.*, 1934, 18, 1117.

nitrogen into  $N_2^+$  ions, and CO into  $CO^+$  ions, and in this form all these gases are rapidly adsorbed even by magnesium. Gettering during the dispersal of the metal is more effective when it is carried out slowly, on account of the fresh surface which is continually being formed.

These adsorptions to be effective for the purpose in view must be irreversible with respect to pressure. The adsorbed gas may, however, be desorbed if displaced by another, more strongly adsorbed gas. Thus nitrogen is usually evolved when a barium deposit adsorbs hydrogen. Adsorbed gas is also driven off if the getter surface is bombarded by electrons or positive ions. There is evidence, from the fact that a getter surface may become saturated but recover on resting, that an activated diffusion to the interior of the deposit takes place. A black, porous deposit of barium obtained by decomposition of the azide is a more effective getter than a bright metallic deposit for this reason.

The total amount of gas that can be adsorbed by a getter deposit is equivalent to very many molecular layers on the measured surface, and depends on the thickness of the deposit. The rate of adsorption is increased by raising the temperature of the getter, again indicating that the process is one requiring an activation energy.

The adsorption of gases by evaporated metals on glass surfaces cooled to  $-183^\circ\text{C}$ . shows somewhat different characteristics. Frankenburger<sup>1</sup> found, for example, that if iron, evaporated from a hot wire in the presence of hydrogen, was allowed to condense on a glass surface cooled in liquid air, one molecule of hydrogen was cleaned up for each atom of iron condensed. Nitrogen was not cleaned up. Bastow<sup>2</sup> found that under the same conditions both  $H_2$  and  $N_2$  were cleaned up by platinum, again in a molecular ratio. On warming such films to  $0^\circ\text{C}$ ., the whole of the gas is liberated, but is not re-adsorbed on cooling. This must be attributed to the sintering of the film, and consequent reduction in activity. At  $-183^\circ\text{C}$ .

<sup>1</sup> Frankenburger, *Z. Phys. Chem.*, 1928, **139**, 386; *Z. Electrochem.*, 1929, **35**, 9.

<sup>2</sup> Bastow, *J. Chem. Soc.*, 1931, 1950.



the adsorbed nitrogen reacts with both hydrogen and water vapour to give ammonia, but there is no action in contact with the sintered film.

Carbon monoxide is cleaned up by evaporated nickel,<sup>1</sup> two molecules of CO disappearing for each nickel atom at 900° C. CO<sub>2</sub> and nitrogen are not adsorbed. Carbon monoxide is cleaned up in the same way by molybdenum at 1627° C.

<sup>1</sup> Bryce, *J. Chem. Soc.*, 1936, 1513.

## CHAPTER II.

## DIFFUSION.

UNDER suitable conditions, certain gases are able to pass through solid metals. This process is known as diffusion. The earliest observations of this phenomenon were described by Cailletet <sup>1</sup> in 1863. He found that when an iron vessel was immersed in dilute sulphuric acid, the hydrogen was not all evolved at the surface, but some of it passed through the metal and appeared inside the vessel. By making the iron the cathode in an electrolytic cell the rate of diffusion may be very much increased, and diffusion will proceed even when the pressure of hydrogen inside the vessel is as much as 20 atmospheres. If, instead of nascent hydrogen produced in this way, the vessel is surrounded with ordinary molecular hydrogen, no measurable diffusion takes place at room temperature,<sup>2</sup> but if the iron is heated to 350° C. it can readily be detected, and the rate of diffusion increases rapidly as the temperature is raised still further.

In the same year Deville and Troost,<sup>3</sup> whilst trying to find suitable materials for making gas thermometers, discovered that platinum was permeable to hydrogen. Similar evidence regarding the diffusion of hydrogen through palladium was obtained by Graham <sup>4</sup> in 1866. He used a palladium tube 12 mm. in diameter, and with a wall thickness of 1 mm., a hydrogen atmosphere being maintained on the outside of the tube. He found that appreciable diffusion took place at 240° C., and became very rapid at a red heat. Subsequent investigations, of which the most important were those of Reynolds <sup>5</sup> (1874),

<sup>1</sup> Cailletet, *C. Rend.*, 1863, 56, 847.

<sup>2</sup> Charpy and Bonnerot, *ibid.*, 1912, 154, 592.

<sup>3</sup> Deville and Troost, *ibid.*, 1863, 56, 997.

<sup>4</sup> Graham, *Phil. Trans.*, 1866, 156, 399.

<sup>5</sup> Osborne Reynolds, *Manchester Lit. Phil. Soc.*, 1874, 13, 93.

Ramsay <sup>1</sup> (1894), Bellati and Lussana <sup>2</sup> (1890), Winkelmann <sup>3</sup> (1901), and Richardson <sup>4</sup> (1905), confirmed these results, and showed that hydrogen would diffuse through many other metals. It is now known that hydrogen, oxygen, nitrogen, and possibly some compound gases like CO, can diffuse through a small number of metals, but the rare gases like helium and argon do not diffuse through any metal. The diffusion of oxygen through silver was first shown experimentally by Troost <sup>5</sup> in 1884. The removal of carbon, sulphur and phosphorus by the action of hydrogen on steel at a red heat provides further evidence of the passage of gases through solid metal.<sup>6</sup> It is also well known that gases can be extracted from practically all metals by heating them in vacuo, which necessarily involves diffusion through the metal.

The early experiments showed that the rate of diffusion increased rapidly with the temperature of the metal, and was also dependent on the pressure of the gas, but they were not sufficiently accurate to enable the laws of diffusion to be formulated. This was first seriously attempted by Winkelmann in 1901-5, who put forward certain empirical equations relating to the rate of diffusion with temperature and pressure. At the same time, Richardson, Nicol and Parnell <sup>7</sup> developed a diffusion equation from theoretical considerations, which was strongly supported by experiments on the diffusion of hydrogen through platinum. Subsequent investigations of a large number of gas-metal systems by other workers have confirmed the general form of the Richardson equation, although certain corrections are necessary to make it apply accurately at low temperatures and pressures, and considerable developments have taken place in the theory of the diffusion process. Before considering these, some of the experimental methods used may be described.

<sup>1</sup> Ramsay, *Phil. Mag.*, 1894, 38, 206.

<sup>2</sup> Bellati and Lussana, *Atti del Reale Inst. Veneto Sci.*, 1890, 1, 1173.

<sup>3</sup> Winkelmann, *Ann. Physik*, 1901, 6, 104; 1905, 17, 591; 1906, 19, 1045.

<sup>4</sup> Richardson, Nicol and Parnell, *Phil. Mag.*, 1904, 8, 1.

<sup>5</sup> Troost, *C. Rend.*, 1884, 98, 427.

<sup>6</sup> Charpy and Bonnerot, *ibid.*, 1913, 156, 394.

<sup>7</sup> *Loc. cit.*

## Experimental Methods.

The apparatus used in experiments on the diffusion of nascent hydrogen produced by electrolysis is generally very simple, and a typical form<sup>1</sup> is shown in Fig. 44. The metal tube D is connected by glass tubing to a manometer M, and

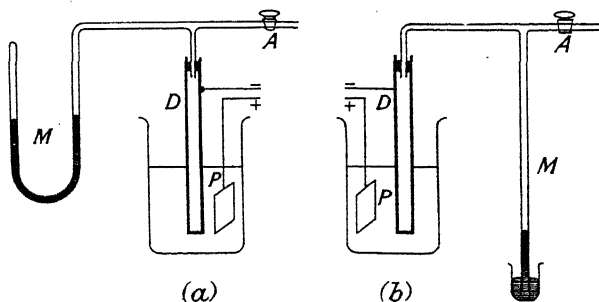


FIG. 44.—Electrolytic diffusion apparatus.

by the tap A to a diffusion pump. The beaker is filled with a 1 per cent. solution of sulphuric acid or caustic soda, a platinum plate is made the anode whilst the metal tube is connected to the negative terminal of a battery. The apparatus is evacuated by means of the pump, the tap A is closed, and the electrical circuit completed. Electrolysis is carried out at a current density of the order of 0.01 ampere per cm.<sup>2</sup>, and the quantity of hydrogen diffusing through the metal tube determined from the change in pressure registered by the manometer. The pressure of molecular hydrogen inside the tube does not affect the rate of diffusion, so that no correction is necessary for the change in pressure during the experiment. With this form of apparatus the effects of current density, applied voltage, and internal gas pressure have been investigated for a number of metals. The modified form of the

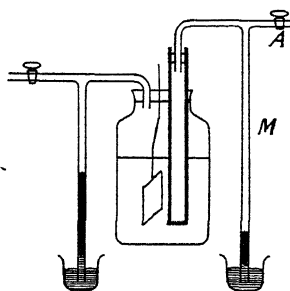


FIG. 45.—Apparatus for electrolytic diffusion under pressure.

<sup>1</sup> Borelius and Lindblom, *Ann. Physik*, 1927, 82, 201.

apparatus shown in Fig. 45 enables the effect of hydrostatic pressure outside the tube to be studied.

Several forms of apparatus have been used in experiments on diffusion from gas in the molecular state. If the metal is available as sheet, a disc can be mounted as a diaphragm in a steel tube, as shown in Fig. 46. The steel tube and specimen *D* are heated by a furnace *F*, and the temperature determined by a thermocouple *T*. The ends of the tube are water-cooled to enable connection to be made to a gas supply by the tap *B*, and to a mercury pump by tap *A*. The pressure of gas on the right-hand side is read from the manometer *M*, and the gas which has diffused can either be continuously pumped away through *A* and measured, or determined from

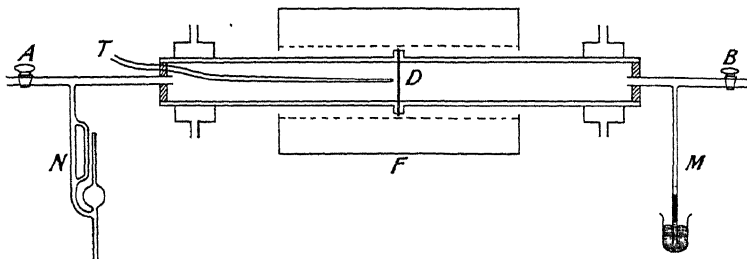


FIG. 46.—Diffusion apparatus.

the increase in pressure recorded by the McLeod gauge *N*, if the tap *A* is kept closed. The chief disadvantages of this method are the difficulty of making such an apparatus really vacuum tight, and errors arising from adsorption on the necessarily large area of the low-pressure side. On the other hand, it is possible to maintain the specimen at a uniform temperature over the whole of its area. This type of apparatus has been used by Johnson and Larose,<sup>1</sup> Lombard,<sup>2</sup> and Ham.<sup>3</sup>

Some of the disadvantages of the previous method can be avoided if the metal is available in the form of thin-walled tubing. Fig. 47 shows the general arrangement of Richardson's apparatus for the diffusion of hydrogen through platinum.

<sup>1</sup> Johnson and Larose, *J. Amer. Chem. Soc.*, 1927, 49, 312.

<sup>2</sup> Lombard, *C. Rend.*, 1923, 177, 116.

<sup>3</sup> Ham, *J. Phys. Chem.*, 1933, 1, 476.

The platinum tube D, 180 mm. long, 2 mm. in diameter, and 0.1 mm. wall thickness, was sealed at either end to glass tubing and could be connected by the 3-way tap A either to the pump or the hydrogen reservoir. After admitting hydrogen the pressure was adjusted by means of the mercury column N.

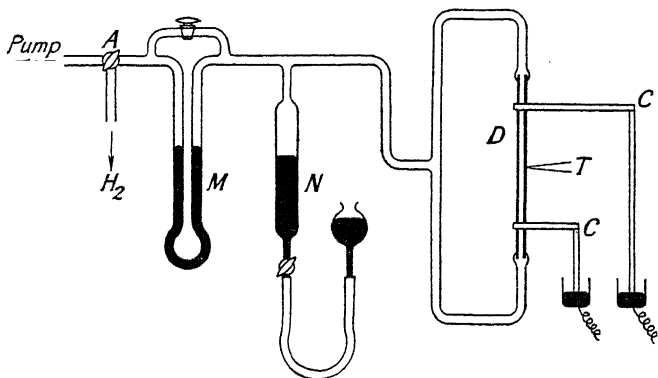


FIG. 47.—Richardson's diffusion apparatus.

The platinum tube was heated by passing an electric current through it from brass contact strips CC. The change in pressure due to hydrogen diffusing outwards through the walls of the tube was read on the manometer M. Whilst measurements can be made over a wide range of temperature and

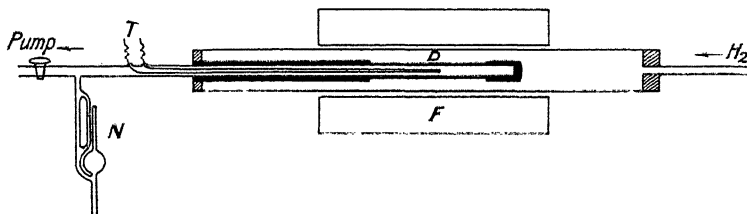


FIG. 48.—Borelius and Lindblom's diffusion apparatus.

pressure, readings cannot be taken at very low pressures, and the temperature of the tube is not uniform throughout its length. Another method is illustrated in Fig. 48. Here the metal tube is sealed at one end and evacuated, the gas being allowed to diffuse from the outside of the tube. This enables

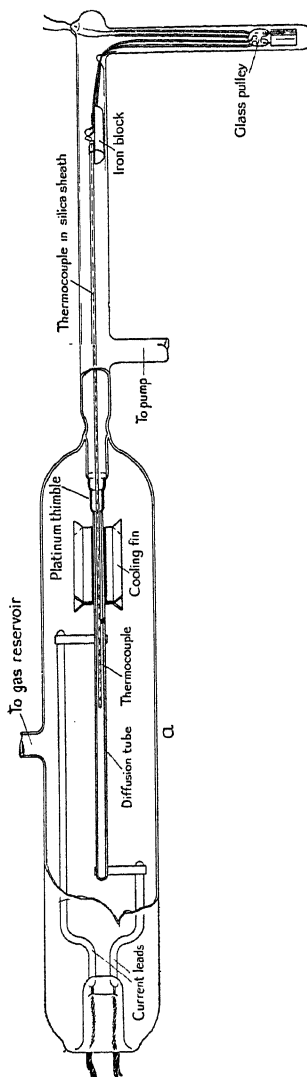


FIG. 49.—Diffusion bulb with exploring thermocouple.

small changes in pressure to be measured accurately by means of the McLeod gauge. Diffusion is confined to a known area in the central part of the furnace F, where the wall of the tube is much reduced in thickness. Smithells and Ransley<sup>1</sup> have used the apparatus shown in Fig. 49, in which the chief disadvantages of the other forms have been overcome.

This consists of a diffusion tube, about 2 mm. in diameter, sealed at one end and continuously evacuated at the other, the gas pressure being maintained on the outside. The tube is heated by passing an electric current through it, by means of two heavy current leads. To obtain a uniform temperature, and avoid end effect, the diameter of the leads in contact with the tube is reduced, so that they are heated to the same temperature as the tube. Tubes of practically any metal may be soldered at their open ends to platinum thimbles, and can then be sealed directly to the glass tube leading to the pump. A radiating fin is provided, so that diffusion is confined to that part of the tube between the electrical leads. The temperature of the tube is

<sup>1</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1935, 150, 172.

measured by the thermocouple inserted down the diffusion tube, and attached to an iron block, which can be moved to and fro with a magnet, so that the temperature at any point in the tube can be measured. The gas pressure on the outside of the tube is maintained sensibly constant by having a large reservoir. A very convenient method of introducing pure hydrogen is by diffusion through a palladium tube, the arrangement being shown in Fig. 50. The palladium tube, 1 mm. bore, and 50 mm. long, is heated by a coil of nichrome wire wound on a silica tube F, through which a stream of hydrogen is passed. With the tube at 800° C. hydrogen diffuses through at the rate of

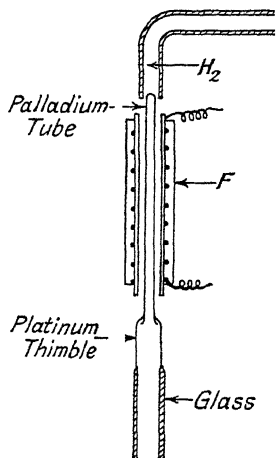


FIG. 50.—Palladium tube for introducing hydrogen.

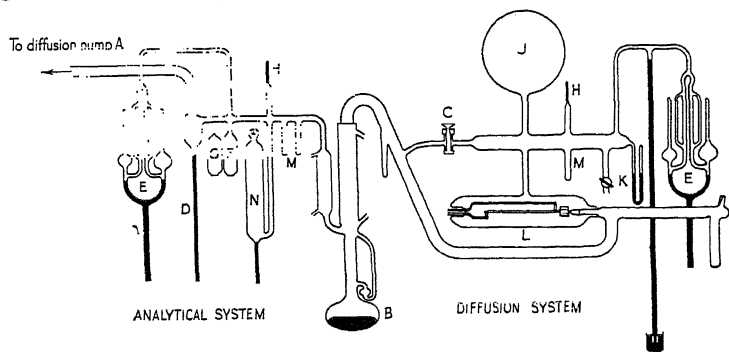


FIG. 51.—Smithells and Ransley's diffusion apparatus.

- |                   |                     |                     |
|-------------------|---------------------|---------------------|
| B diffusion pump  | G compensator       | L diffusion bulb.   |
| D mercury cut-off | HH palladium tubes  | MM freezing tubes.  |
| EE McLeod gauges  | J reservoir         | N compression bulb. |
| F Pirani gauge    | K to gas reservoirs |                     |

about 5 c.c. per min. Oxygen may be introduced in a similar manner if a silver tube is used. Other gases may be supplied from reservoirs permanently sealed to the apparatus.

The complete arrangement is shown in Fig. 51, and consists



of two portions, the diffusion system and the analytical system. The gas pressure in the diffusion bulb is measured by suitable McLeod gauges E. A high vacuum is maintained on the inside of the diffusion tube by the mercury diffusion pump B, and the gas diffusing is collected in the analytical system between this pump and the mercury cut-off D. It is always desirable to check by analysis that the gas collected is actually that under investigation. In experiments with the noble gases, for example, a small quantity of gas is usually collected, which proves to be hydrogen, either present as an impurity in the gas, or evolved from some part of the apparatus. Compound gases frequently decompose and only one constituent, for

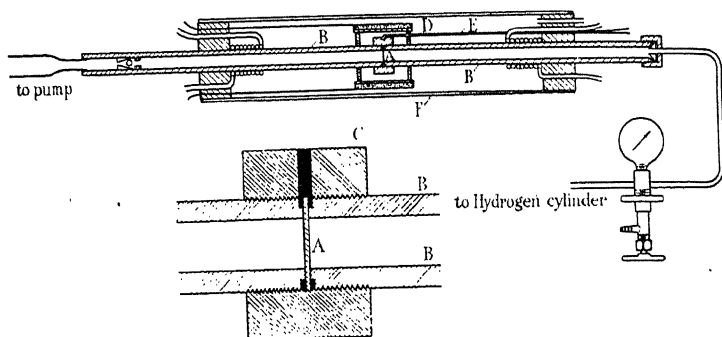


FIG. 52.—Apparatus for diffusion at 100 atmospheres pressure.

example hydrogen, actually diffuses through the metal. In the absence of analysis, this has often led to the false conclusion that compound gases may diffuse through metals without dissociation. Although the pressure developed in the analytical system may not exceed  $10^{-3}$  mm., satisfactory methods of micro-analysis are available.<sup>1</sup>

This apparatus, which has a minimum number of glass taps, can be completely evacuated to a pressure of  $10^{-6}$  mm. of mercury, and is suitable for diffusion measurements at gas pressures from 1 atmosphere down to  $10^{-3}$  mm. For pressures between 1 atmosphere and 100 atmospheres the diffusion bulb is replaced by the arrangement shown in Fig. 52. The

<sup>1</sup> Campbell, *Proc. Phys. Soc.*, 1921, 33, 287.

diaphragm A is clamped and brazed between the faced ends of two thick walled tubes B, capable of withstanding the high pressure. The diaphragm is heated by the small electric furnace D, and its temperature measured by the thermocouple E. The nickel tubes, water cooled at each end, are surrounded by a metal jacket F, which is evacuated to prevent indirect diffusion through the walls of the tube, and whose ends are connected respectively to the gas supply and the diffusion pump as before.

### Theories of Diffusion.

In considering the diffusion process, we have first to consider the state of the gas whilst passing through the metal. The fact that nascent hydrogen, produced by electrolysis at the surface of a metal, diffuses far more rapidly than molecular hydrogen at the same temperature, indicates that the gas may only diffuse in the atomic state. This view was first put forward by Ramsay,<sup>1</sup> and has been supported by subsequent experiments, although direct evidence of its truth has only been obtained quite recently. This is fully discussed on page 96. The second question which arises is how the gas atoms pass through the metal, and what paths they follow. The most obvious alternatives are that the gas passes between the metal atoms—lattice diffusion—or is confined solely to the boundaries between the metal crystals—grain boundary diffusion. The evidence, which shows that diffusion normally takes place through the lattice, will be considered in detail later. The effects of different variables on the diffusion of gases through metals have been studied with a view to solving these problems and understanding the mechanism of the diffusion process. We may record at once that diffusion is specific, and that any particular gas will only diffuse through certain metals. Graham's Law, that the rate of diffusion is inversely proportional to the square root of the density of the gas, does not hold for the diffusion of gases in metals. The most important variables are the temperature of the metal, the pressure of gas on each side, and the thickness

<sup>1</sup> *Loc. cit.*

of the metal. Other factors whose influence is less apparent, but of considerable importance, are the structure of the metal and the physical state of the surface. We will consider each of these variables in turn.

### Effect of Thickness.

Fick's linear diffusion law may be applied to the diffusion of a gas within a metal. This may be expressed by the equation

$$\frac{dS}{dt} = \Delta \frac{dc}{dx} \quad (13)$$

where  $dS$  is the quantity of gas diffusing in time  $dt$ ,  $\frac{dc}{dx}$  is the

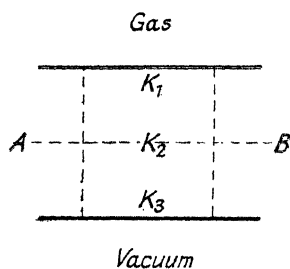


FIG. 53.

concentration gradient, and  $\Delta$  is the diffusivity constant. The rate of change of concentration at any point is given by the equation

$$\frac{dc}{dt} = \Delta \frac{d^2c}{dx^2}.$$

Since the rate of diffusion is proportional to the concentration gradient, it will under any given conditions of temperature and pressure be inversely proportional to the thickness of the metal.

Fig. 53 represents a section through a sheet of metal, one side of which is in contact with the gas whilst a vacuum is maintained on the other side. The line AB represents a surface half-way through the metal. It is clear that if the thickness of the metal is halved the concentration gradient will be doubled and so also will the rate of diffusion. Johnson and Larose<sup>1</sup> determined the rate of diffusion of oxygen through silver foil of various thicknesses between 0.07 and 0.25 mm. The rates of diffusion plotted against the inverse of the thickness give a straight line, as shown in Fig. 54. Similar results have been obtained for the diffusion of hydrogen through

<sup>1</sup> Johnson and Larose, *J. Amer. Chem. Soc.*, 1924, 46, 1377.

nickel<sup>1</sup> and iron<sup>2</sup> In quoting rates of diffusion it is usual to refer to some standard thickness. It is most convenient to express the rate of diffusion  $D$  as the volume of gas in cubic

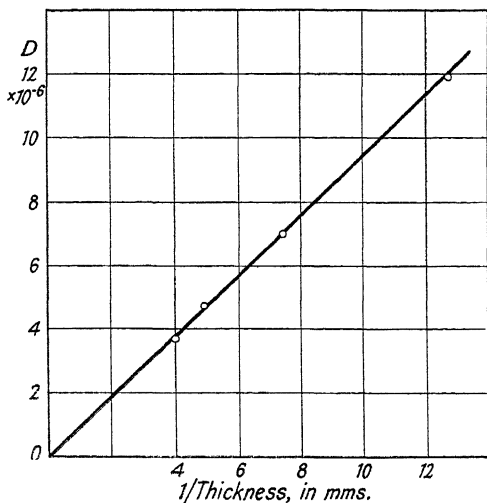


FIG. 54.—Effect of thickness on rate of diffusion of oxygen through silver.

centimetres at N.T.P. diffusing per second through 1 square centimetre of surface of 1 mm. thickness. The values of  $D$  given in this chapter are expressed in these units.

### Effect of Temperature.

Experiment shows that the rate of diffusion increases very rapidly with temperature. Some typical diffusion curves are shown in Fig. 55, where the rate of diffusion is plotted against the temperature. Numerous attempts were made to find an equation which would represent the experimental results. Winkelmann found that an equation of the form

$$D = aT^b,$$

where  $a$  and  $b$  were constants, represented his results for the diffusion of hydrogen through iron,  $b$  having a value of

<sup>1</sup> Lombard, *C. Rend.*, 1923, 177, 116.

<sup>2</sup> Lewkonja and Baukloh, *Z. Metallk.*, 1933, 25, 309.

about 5. Johnson and Larose applied this equation to their observations of the diffusion of oxygen through silver, and found close agreement with  $b = 14.6$ . Another empirical equation of the form

$$D = ab^T$$

was proposed by Lombard, which was in good agreement with experimental results for the diffusion of hydrogen through nickel. Richardson, however, from theoretical considerations, arrived at an equation for diffusion of the following form :

$$D = K \cdot \frac{I}{d} \cdot p^{\frac{1}{2}} \cdot T^{\frac{1}{2}} \cdot e^{-\frac{q}{T}} \quad (14)$$

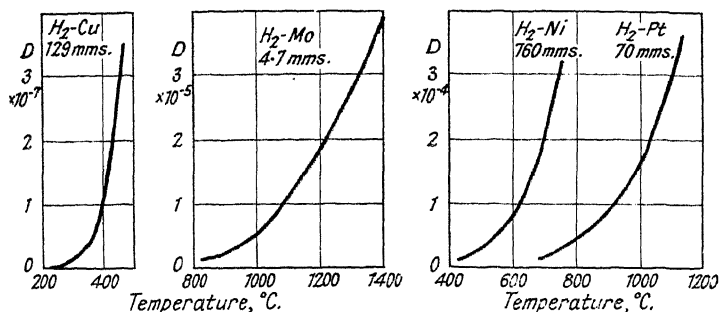


FIG. 55.—Typical diffusion isobars.

in which, to a first approximation, the effect of temperature is represented by

$$D = a \cdot e^{-\frac{q}{T}} \quad (15)$$

Each of these equations appeared to be supported by experiment because, if suitable values for the constants are selected in each case, the equations give very similar results over a limited range of temperature. If we take a series of experimental observations and plot the logarithm of the rate of diffusion  $D$ , against the logarithm of the absolute temperature  $T$ , we should obtain a straight line if Winkelmann's equation is correct. If Lombard's equation is right the points should fall on a straight line when  $\log D$  is plotted against  $T$ , whereas Richard-

son's equation demands that  $\log D$  should be proportional to  $\frac{1}{T}$ . In

Fig. 56 experimental results for the diffusion of hydrogen through iron have been plotted in each of these ways, and it will be seen that

the results strongly support equation (15). The effect of tem-

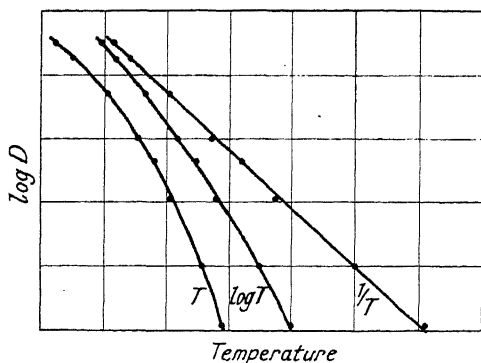


FIG. 56.

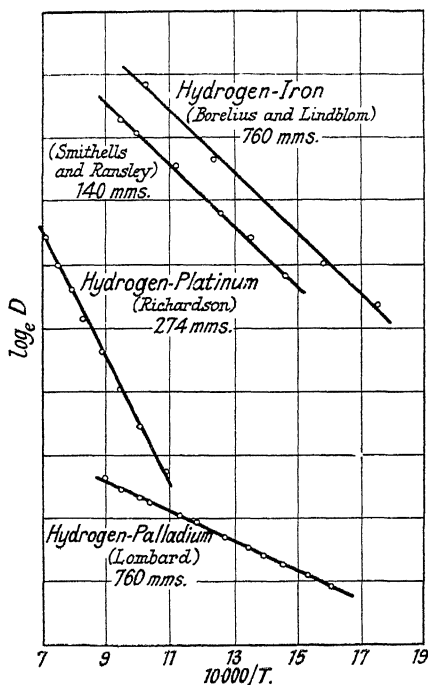


FIG. 57.

perature on the rate of diffusion is shown for a number of other gas-metal systems in Figs. 57 to 60, where  $\log D$  is plotted against  $1/T$ . In each case the observations lie sufficiently closely on straight lines to leave little doubt that the exponential equation satisfactorily represents the effect of temperature on diffusion, within the limits of experimental error.

The original derivation of this equation by Richardson can no longer be considered quite satisfactory, and certain necessary data regarding the exchange of energy at the surface

of the metal are still lacking. An approximate equation can, however, be derived by purely thermodynamical reasoning in the following manner.<sup>1</sup>

As will be seen later, energy exchanges which take place at the surface of the metal have an important bearing on diffusion, although exact knowledge is at present lacking. In the follow-

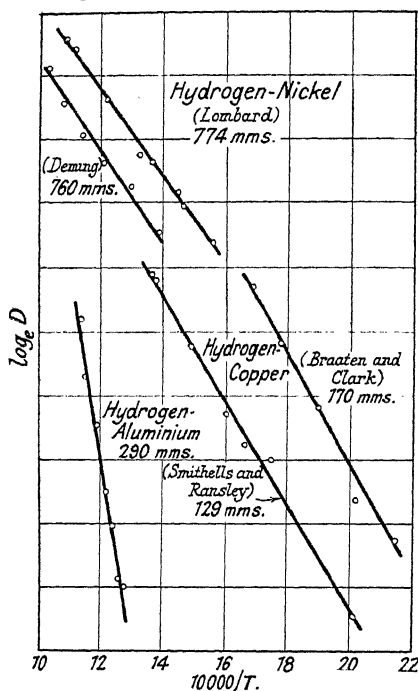


FIG. 58.

ing argument such exchanges of energy are ignored, and the equation derived is therefore only valid when no appreciable change occurs in the amount of gas adsorbed on the surface. A further assumption is made, that the rate of diffusion through the metal is sufficiently slow to allow the concentration of gas, immediately below the surface of the metal, to be maintained substantially in equilibrium with the gas outside. This assumption is probably only true for certain cases.

Consider a system of  $n_0$  atoms of solid metal,  $n_1$  atoms of dissolved gas,  $n_0'$  atoms of metal vapour, and  $n_1'$  molecules (diatomic) of free gas, with

$$n_1 < n_0 \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$n'_0 < n_1 \quad (17)$$

<sup>1</sup> I am indebted to my colleague Dr. A. L. Reimann for this derivation of the Richardson formula.

Then, from thermodynamics, the condition for this system to be in equilibrium is that for a virtual transference of molecules

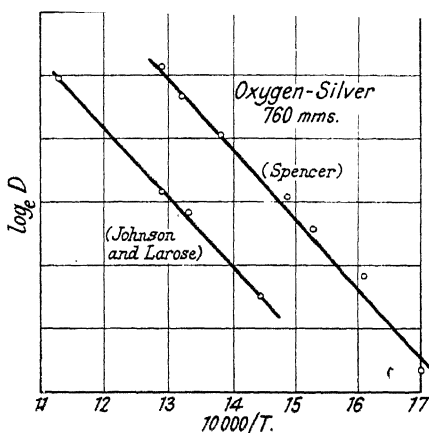


FIG. 59.

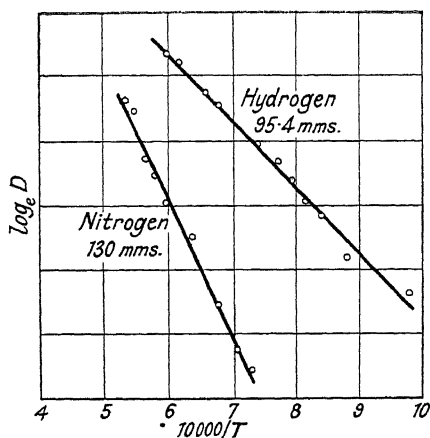


FIG. 60.—Diffusion of hydrogen and nitrogen through molybdenum.

[Smithells and Ransley.

from one phase to another at the given temperature and pressure, the relation

$$C_0^{\delta n_0} C_1^{\delta n_1} C_0'^{\delta n_0'} C_1'^{\delta n_1'} = K' \quad . \quad . \quad (18)$$



must hold, where by definition

$$C_0 = \frac{n_0}{n_0 + n_1}, \quad C_1 = \frac{n_1}{n_0 + n_1}, \quad C_0' = \frac{n_0'}{n_0' + n_1'}, \quad C_1' = \frac{n_1'}{n_0' + n_1'},$$

and  $K'$  is a quantity the partial derivatives of whose logarithm with respect to  $T$  and  $p$  are

$$\frac{\partial \log K'}{\partial T} = \frac{Q}{kT^2} \quad . \quad . \quad . \quad (19)$$

$$\text{and} \quad \frac{\partial \log K'}{\partial p} = -\frac{\delta V}{kT} \quad . \quad . \quad . \quad (20)$$

where  $k$  is Boltzmann's constant,  $Q$  is the quantity of heat that would have to be supplied to the system to bring about the change, and  $\delta V$  is the amount by which its total volume would increase.

In the case under consideration, we are interested merely in the equilibrium between the dissolved and undissolved gas, so that we need not consider a virtual transference of metal particles between the two phases, and it will be convenient to set  $\delta n_0 = \delta n_0' = 0$ ,  $\delta n_1 = -2$ , and correspondingly  $\delta n_1' = 1$ . From (17) we see that  $C_1'$  is practically equal to 1. The equilibrium condition then reduces to

$$C_1^{-2} = K' \quad . \quad . \quad . \quad (21)$$

$Q$  now becomes the quantity of heat that must be supplied to the system at constant temperature and pressure to diminish the number of dissolved gas atoms by 2, thereby increasing the number of gas molecules in the gas phase by 1, and the right-hand side of (20) becomes  $-\frac{1}{p}$ .

To evaluate  $K'$  it is necessary to integrate (19) and (20). Before we can integrate (19) we must know what function  $Q$  is of  $T$ . From the first law of thermodynamics we have

$$\frac{\partial Q}{\partial T} = \frac{1}{N} (C_p' - 2C_p) \quad . \quad . \quad . \quad (22)$$

where  $N$  is Avogadro's number, and  $C_p'$  and  $C_p$  are the molecular heats at constant pressure of the undissolved and the

dissolved gas respectively. The factor 2 arises from the dissociation. The quantity  $\frac{C_p'}{N}$  is known for a diatomic gas to be

$\frac{7}{2}k$ . About  $C_p$ , however, we cannot be so sure. If a gas atom

in the metal had the same thermal energy as a lattice atom,  $\frac{C_p}{N}$  would be about  $3k$ , and this is the most probable value in the light of present knowledge. In general, however, we can write

$$\frac{C_p}{N} = \alpha k \quad . \quad . \quad . \quad . \quad (23)$$

assuming  $\alpha$  to be a constant, at least over the range of temperatures considered. Making the appropriate substitutions in (22) and integrating, we then have

$$Q = \psi \left( \frac{7}{2} - 2\alpha \right) kT \quad . \quad . \quad . \quad (24)$$

where  $\psi$  is a constant of integration.

Substituting (24) in (19), and  $\frac{1}{p}$  for  $\frac{\delta V}{kT}$  in (20), and integrating both equations, we obtain

$$\log K = -\log p + \left( \frac{7}{2} - 2\alpha \right) \log T - \frac{\psi}{kT} + \text{const.} \quad (25)$$

and combining this with equation (21),

$$C_1 = ap^{\frac{1}{2}} T^{\frac{7}{2} - 2\alpha} e^{-\frac{\psi}{2kT}} \quad . \quad . \quad . \quad (26)$$

where  $a$  is a new constant.

We now have to consider diffusion within the metal. Let  $c_1$  and  $c_2$  be the concentrations of gas near the two surfaces of a plate of thickness  $d$ . Then the concentration gradient will be proportional to  $\frac{c_1 - c_2}{d}$ , and so also will the rate of diffusion  $D$ . Let the activation energy of diffusion be  $E$ , then  $D$  will also be proportional to  $e^{-\frac{E}{2kT}}$ . The values of  $c_1$  and  $c_2$

will be determined by the gas pressures  $p_1$  and  $p_2$  on the two sides of the plate according to equation (26), and we have finally

$$D = \frac{K}{d} \cdot (\sqrt{p_1} - \sqrt{p_2}) T^{(\alpha - \frac{7}{4})} e^{-\frac{E - \psi}{2kT}},$$

where  $K$  is the diffusion constant. If a vacuum is maintained on one side of the plate  $p_2 = 0$ , and putting  $E - \psi = E_0$ , and giving  $\alpha$  its most probable value of 3, we have

$$D = \frac{K}{d} \cdot p^{\frac{1}{2}} T^{\frac{5}{4}} e^{-\frac{E_0}{2kT}}.$$

This is the same form as Richardson's original equation except for the power of  $T$ . This term is, however, insignificant compared with the exponential and may for practical purposes be neglected, so that the simplified equation becomes

$$D = \frac{K}{d} \sqrt{p} \cdot e^{-\frac{E_0}{2kT}}. \quad (27)$$

The values of  $K$  and  $E_0$  found by different observers for a large number of gas-metal systems are collected in Table 9. The values of  $E_0$  in calories per gram molecule of gas are obtained from the slope of the  $\log D - \frac{1}{T}$  plots, since from equation (27)

$$\log_e D = \frac{E_0}{2kT}.$$

This table brings out the rather remarkable uniformity in the value of the diffusion constant for such different systems as hydrogen-palladium, oxygen-silver and nitrogen-molybdenum. For all systems where diffusion can be measured at all the value does not vary by as much as 100 to 1. The extreme variation in the value of the heat of diffusion is about 10 to 1. Considering hydrogen only, and excluding the rather exceptional case of palladium, the value of  $E_0$  only varies by 2 to 1. These values are of the same order—10,000

to 20,000 cal./mol.—as the heats found for activated adsorption (p. 48).

TABLE 9.

DIFFUSION CONSTANTS IN EQUATION  $D = K \cdot \frac{1}{d} \cdot p^{\frac{1}{2}} e^{-\frac{E_0}{2kT}}$  c.c./cm.<sup>2</sup>/sec./mm.

System.	$E_0$ Cals./Grm. Mol.	K.	Reference.
$H_2$ —Ni	30,840	$2.3 \times 10^{-2}$	Lombard
	27,720	$0.85 \times 10^{-2}$	Deming and Hendricks
	27,600	$1.4 \times 10^{-2}$	Borelius and Lindblom
	26,800	$1.05 \times 10^{-2}$	Ham
	26,520	$1.44 \times 10^{-2}$	Smithells and Ransley
$H_2$ —Pt	39,200	$1.41 \times 10^{-2}$	Richardson
	36,000	$1.18 \times 10^{-2}$	Ham
$H_2$ —Mo	40,400	$0.93 \times 10^{-2}$	Smithells and Ransley
$H_2$ —Pd	8,400	$4.1 \times 10^{-2}$	Lombard and Eichner
	8,900	—	Melville and Rideal
$H_2$ —Cu	33,200	$2.3 \times 10^{-3}$	Smithells and Ransley
	39,400	$1.5 \times 10^{-3}$	Braaten and Clark
$H_2$ —Fe	19,200	$1.63 \times 10^{-3}$	Smithells and Ransley
	18,800	$1.60 \times 10^{-3}$	Borelius and Lindblom
	22,000	$2.40 \times 10^{-3}$	Ryder
$H_2$ —Al	61,600	3.3 to 0.42	Smithells and Ransley
$O_2$ —Ag	45,200	$3.75 \times 10^{-2}$	Spencer
	45,200	$2.06 \times 10^{-2}$	Johnstone and Larose
$N_2$ —Mo	90,000	$8.3 \times 10^{-2}$	Smithells and Ransley
$N_2$ —Fe	47,600	$4.5 \times 10^{-3}$	Ryder
CO—Fe	37,200	$1.3 \times 10^{-3}$	Ryder

### Effect of Gas Pressure.

The rate of diffusion of gases through metals increases as the gas pressure is increased, but not in a manner directly proportional to the pressure. Some typical diffusion isotherms

are shown in Fig. 61 where the rate of diffusion is plotted against the pressure. If the gas diffused through the metal in the molecular state we should expect the rate of diffusion to be directly proportional to the gas pressure—that is, to the number of gas molecules striking the surface per second. When air, for example, is forced through a tube packed with Kieselghur the rate of flow is found to be proportional to the pressure. The rate of diffusion of gases through glass and silica is also directly proportional to the pressure, the very open spacing of the  $\text{SiO}_2$  lattice permitting diffusion as a purely physical process.<sup>1</sup>

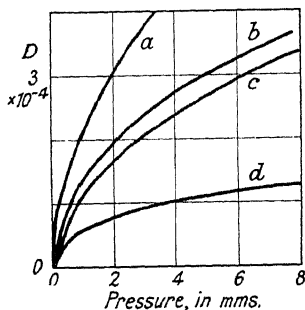


FIG. 61.—Typical diffusion isotherms for hydrogen.

- (a) Molybdenum at  $1400^{\circ}\text{C}$ .
- (b) Platinum at  $1136^{\circ}\text{C}$ .
- (c) Iron at  $702^{\circ}\text{C}$ .
- (d) Nickel at  $587^{\circ}\text{C}$ .

The fact that diffusion is not proportional to the pressure in the case of metals indicates that the substance diffusing is probably not molecular hydrogen, but hydrogen in some other form, possibly atomic. Further evidence pointing in this direction is found in the diffusion of nascent hydrogen, produced electrolytically, against a pressure of as much as 20 atmospheres of molecular hydrogen inside an iron vessel.

Although Ramsay first suggested that hydrogen probably diffused in the atomic or dissociated state, he did not explain how this would account for the observed results, and the effect of pressure was first seriously investigated by Winkelmann.<sup>2</sup>

He set out to determine the effect of pressure on the rate of diffusion of hydrogen through a palladium tube, and later repeated his experiments with a platinum tube. The apparatus used was not capable of giving very accurate results, but he established clearly that the rate of diffusion was certainly not directly proportional to the gas pressure, and did

<sup>1</sup> Barrer, *J. Chem. Soc.*, 1934, 378; Braaten and Clark, *J. Amer. Chem. Soc.*, 1935, 57, 2714.

<sup>2</sup> Winkelmann, *Ann. Physik*, 1901, 6, 104; 1902, 8, 388.

not diminish as fast as would be expected when the pressure was reduced. To explain these results he suggested that the hydrogen was dissociated to a certain extent, and that only that part of the hydrogen which was present in the gas as atoms could diffuse. If  $p_2$  represents the pressure of molecular hydrogen and  $p_1$  the pressure of dissociated atoms, then the gas pressure  $p = p_1 + p_2$ . From the law of mass action

$$p_1^2 = k,$$

where  $k$  is a constant, and from these two equations

$$p_1 = \sqrt{k} \quad p + \frac{k}{4} = \frac{k}{4}.$$

Therefore, if the rate of diffusion  $D$  is proportional to the pressure of the dissociated gas,

$$D = A(\sqrt{p + a} - \sqrt{a}) \quad . \quad . \quad . \quad (28)$$

This equation was in reasonable agreement with experimental results when suitable values of  $A$  and  $a$  were chosen.

Richardson showed, however, that the rate of diffusion of hydrogen through platinum was far higher than could be accounted for by the known dissociation of the gas at the temperatures in question. He suggested that the equation

$$D = k\sqrt{p} \quad . \quad . \quad . \quad . \quad (29)$$

represents the observed results within the experimental error (about 3 per cent.) when the gas pressure on one side of the diaphragm is  $p$  and a vacuum is maintained on the other side. He assumed that the gas was completely dissociated inside the metal, and was in equilibrium with molecular hydrogen outside the metal. This would lead to equation (29) from a consideration of the laws of mass action.

This conclusion was generally accepted for nearly a quarter of a century, but was challenged in 1927 by Borelius and Lindblom.<sup>1</sup> They showed by very careful measurements of the rate of diffusion of hydrogen through iron and nickel that,

<sup>1</sup> *Loc. cit.*

particularly at low temperatures, the simple  $\sqrt{p}$  law did *not* represent the observed results within the experimental error. An empirical equation of the form

$$D = k(\sqrt{p} - \sqrt{p_t}) \quad . \quad . \quad . \quad (30)$$

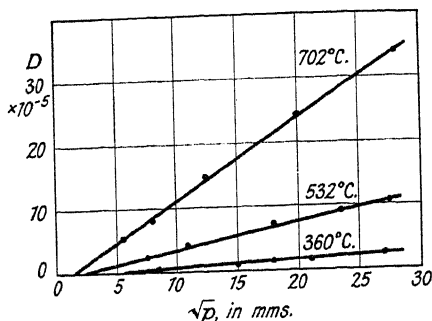


FIG. 62.—Hydrogen—iron.

[Borelius and Lindblom.

gave closer agreement, not only with their own observations but also with those of Richardson. Some of their observations are shown in Fig. 62 where the rate of diffusion is plotted against  $\sqrt{p}$ . The points lie on substantially straight lines which, however, do not go through the origin, but cut the pressure axis at small positive values. This value  $p_t$ , which varied with temperature, was considered to be a threshold value of pressure below which no diffusion took place, and was tentatively attributed to the effect of grain boundaries.

A more careful examination of published data by Smithells and Ransley,<sup>1</sup> together with accurate measurements at low pressures for a number of gas metal systems, confirmed the deviation from the square root law at low pressures, but not the existence of any threshold value. The rate of diffusion at low pressures falls off more rapidly than is required by proportionality to  $\sqrt{p}$ , but is still measurable at pressures

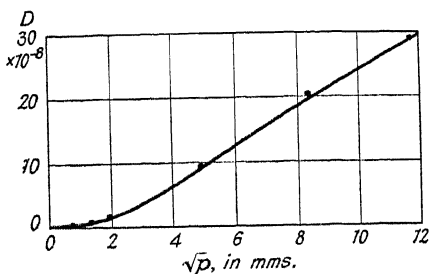


FIG. 63.—Hydrogen—copper at 450° C.

[Smithells and Ransley.

<sup>1</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1935, 150, 172.

below  $10^{-1}$  mm. They suggested that the deviation probably depended on  $\theta$ , the fraction of the surface covered by adsorbed gas. An empirical equation of the form

$$D = k\theta\sqrt{p} \quad (31)$$

was found to give good agreement with experimental results for a large number of gas-metal systems. We may express  $\theta$  in terms of  $p$  by means of the appropriate isothermal equation, depending on whether the gas is dissociated

at the surface, or not. At high pressures, when  $\theta$  approaches unity, equation (31) approximates to

$$D = k\sqrt{p},$$

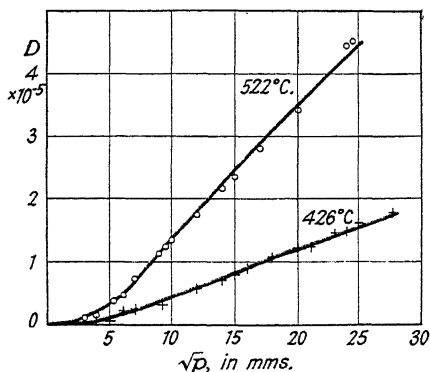


FIG. 65.—Hydrogen—nickel.

[Smithells and Ransley.]

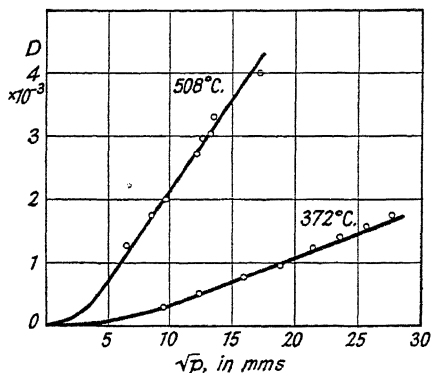


FIG. 64.—Hydrogen—palladium.

[Lombard.]

and agrees with Richardson's equation; but at low pressures the rate of diffusion will fall off more rapidly, in the same way as has been observed experimentally. In Figs. 63 to 70 the observed rates of diffusion for a number of gas-metal systems are plotted against the square root of the gas pressure, for most of

the systems which have been studied. The actual observations are plotted as small circles, and in each case the curve for equation (31) with suitable values selected for the constants  $a$  and  $k$



has been drawn in. The experimental points are in every case well represented by the calculated curve. It should be noted that as the temperature is raised the departure from the simple

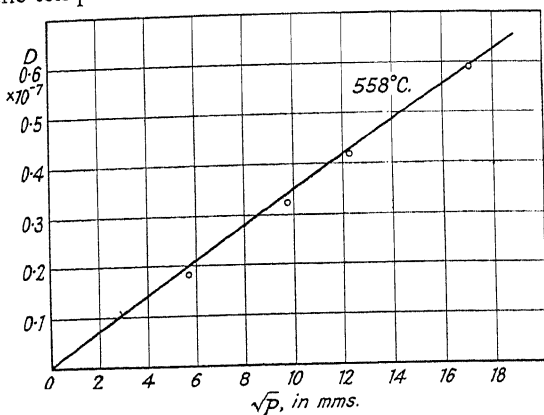


FIG. 66.—Hydrogen—aluminium.

[Smithells and Ransley.

square root relationship becomes less marked, indicating that the surface is more nearly covered by adsorbed gas.

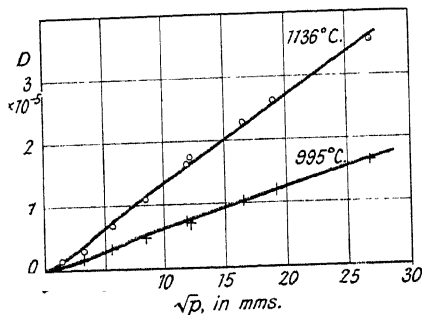


FIG. 67.—Hydrogen—platinum.

[Richardson, Nicol and Parnell.

In a recent paper Braaten and Clark<sup>1</sup> have confirmed the agreement between equation (31) and their measurements of the diffusion of hydrogen through copper. If the experimental results are represented by a graph in which  $\frac{p^{3/2}}{D}$  is plotted against

$p$ , a straight line should result if the equation is accurately obeyed. They point out that both their own results and those of Smithells and Ransley show a small deviation at pressures

<sup>1</sup> Braaten and Clark, *Proc. Roy. Soc.*, 1936, 153, 504.

below 2 mm., as shown in Fig. 71, which would indicate that the amount of gas adsorbed at this pressure is greater than is required by the adsorption isotherm.

It is clear, however, that although this equation represents experimental results very closely, its theoretical basis is unsatisfactory. For if diffusion is proportional to the fraction of the surface covered by adsorbed atoms, then when  $\theta=1$  further increase in pressure should have no effect. Melville and Rideal<sup>1</sup> have developed a

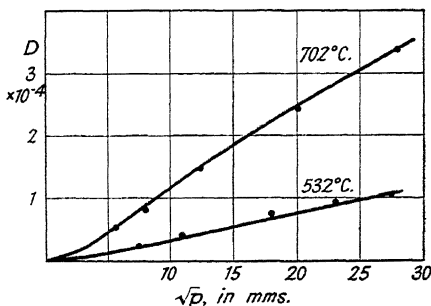


FIG. 68.—Hydrogen—iron.

[Borelius and Lindblom.

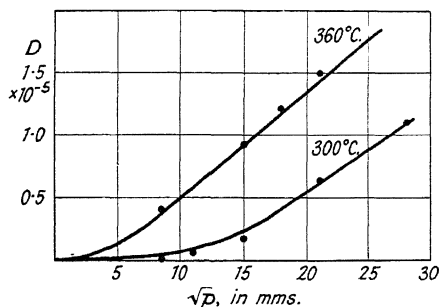


FIG. 69.—Hydrogen—iron.

[Borelius and Lindblom.

pairs of atoms, and the third term due to diffusion through the metal. But since

$$[H_2] = k \frac{ap}{1 + ap} = k\theta,$$

the rate of diffusion should become independent of pressure

<sup>1</sup> Melville and Rideal, *Proc. Roy. Soc.*, 1935, 153, 77 and 89.

<sup>2</sup> See p. 56.

concentration of adsorbed molecules on the surface is  $[H_2]$  and the concentration of hydrogen atoms just inside the metal is  $[H]$ , then at equilibrium

$$k[H_2] - k_2[H]^2 - k_3[H] = 0,$$

the second term being due to evaporation from the surface of

when  $\theta = 1$ , and some evidence of this would be expected at high pressures when  $\theta$  approaches unity.

That the rate of diffusion of hydrogen through iron was

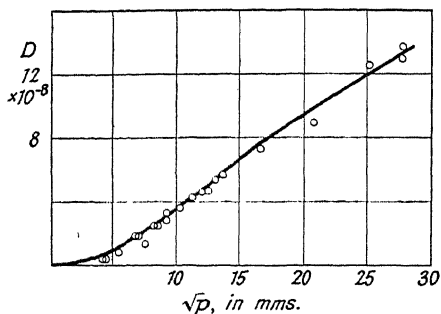


FIG. 70.—Silver—oxygen at 400° C.

[Spencer.]

at temperatures of 248° and 400° C. there is still no sign of departure from the square root law.

So far, in considering the mechanism of diffusion, it has

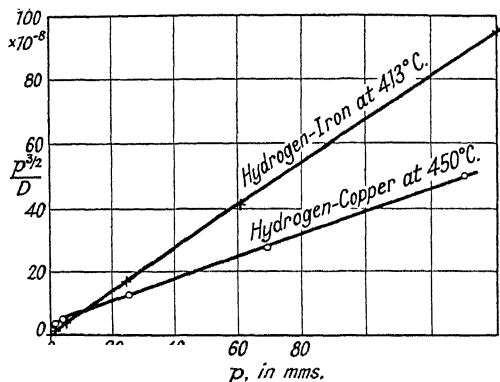


FIG. 71.—Diffusion data plotted to check equation (31).

been assumed that the rate of supply of gas atoms depends solely on the concentration of gas adsorbed on the surface. All the experimental evidence indicates that adsorption is

<sup>1</sup> Borelius and Lindblom, *Annalen der Physik*, 1927, 82, 201.

<sup>2</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1936, 157, 292.

sensibly complete at pressures of the order of 1 atmosphere, and yet diffusion continues to be affected by the pressure, at least to 112 atmospheres. To explain the continued effect of pressure it was suggested<sup>1</sup> that the rate of diffusion at higher pressures might depend mainly on the impact of gas molecules on the adsorbed atoms, and that the necessary activation energy for diffusion might be derived from the kinetic energy of the gas molecules. In our earlier picture of the diffusion process, we assumed that an adsorbed atom remained on the

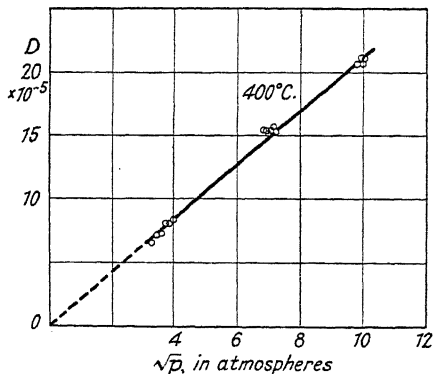


FIG. 72.—Diffusion of hydrogen through nickel at high pressures.

[Smithells and Ransley.

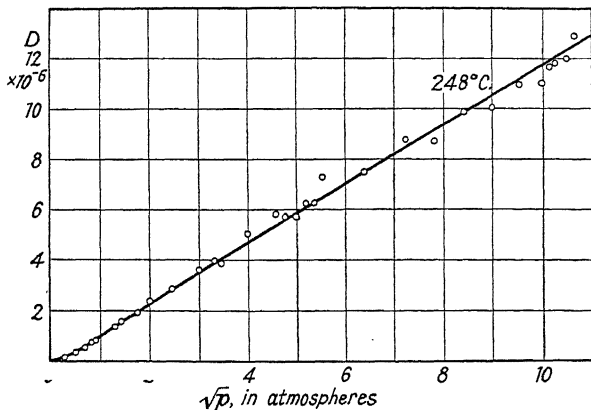


FIG. 73.—Diffusion of hydrogen through nickel up to 112 atmospheres.

[Smithells and Ransley.

surface until it acquired sufficient energy by thermal agitation either to evaporate or to pass into the metal. If, however, the

<sup>1</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1936, 157, 292.

necessary energy can be acquired by the impact of a gas molecule the process will be accelerated, and will, in fact, continue to be a function of the gas pressure even when the surface is completely covered. A simple calculation shows that under the conditions of the high-pressure experiments referred to, there would be a sufficient number of molecules having the required energy, to account for the observed diffusion. The activation energy necessary for the transference of an atom from the surface into the metal is not known exactly, but must be of the order of 5000 cal./gm. mol.<sup>1</sup> At 248° C. and a pressure of 10 atmospheres the number of gas molecules striking 1 cm.<sup>2</sup> of surface per second with an energy exceeding this value is  $1.3 \times 10^{23}$ , whereas the observed rate of diffusion through a thickness of 1 mm. of nickel under these conditions corresponds to only  $1.1 \times 10^{14}$  molecules. There are thus  $10^9$  times the required number of impacts in which a sufficient exchange of energy might take place.

It remains to see whether such a process would give an equation in agreement with experiment. This involves a detailed consideration of all the types of impact that might take place at the surface, for each of which there must also be a corresponding process in the reverse direction.

The following are examples of the kind of processes we have to consider :—

(1) An adsorbed atom passes into the metal.

(1R) The reverse of (1), i.e., an atom diffuses up to the surface and is adsorbed.

(2) A molecule strikes the bare surface, is dissociated and the atoms adsorbed.

(2R) Two adsorbed atoms combine and evaporate as a molecule.

(3) A molecule strikes the bare surface, one atom is adsorbed and one penetrates into the metal.

(3R) An atom diffuses to the surface, combines with an adsorbed atom and evaporates as a molecule.

<sup>1</sup> Melville and Rideal (*loc. cit.*) obtained the value of 2500 cal./gm. mol. for the palladium-hydrogen system.

(4) A molecule strikes the surface where it is covered by adsorbed atoms, two of these enter the surface and the molecule is dissociated and takes their place.

(4R) Two atoms diffuse to adjacent occupied spaces on the surface and displace one molecule.

The reader will find that some dozen different processes, and in each case their reverse, can be imagined. Some of them, like (4R), may be neglected on the grounds of probability. If all types of collision were effective, then as soon as the surface was completely covered increasing the pressure by means of an inert gas should increase the rate of diffusion. Experiment shows, however, that this is not the case. If the rate of diffusion of hydrogen through nickel is measured with a hydrogen pressure of 4 atmospheres (when  $\theta$  must be nearly equal to unity) increasing the pressure to 100 atmospheres by the addition of argon has no effect.<sup>1</sup> This indicates that of the possible types of collision, only those which involve the simultaneous adsorption of the impinging molecule are effective in causing diffusion. This enables us to eliminate a certain number of the possible processes.

We may now write down the contribution of each of the effective processes to the total diffusion, in terms of  $\theta$  and  $p$ . For example, the flows contributed by the processes we have enumerated are given by

$$\begin{aligned} (1) & A\theta_1, \\ (1R) & B\nu_1(1 - \theta_1), \\ (2) & Cp(1 - \theta_1)^2, \\ (2R) & D\theta_1^2, \end{aligned}$$

and so on, where  $A$ ,  $B$ , . . . are temperature dependent constants,  $\theta_1$  refers to the ingoing surface, and  $\nu_1$  is the concentration of H just inside the surface. At the outgoing surface of the metal (the vacuum side) similar processes must be considered, and may be written down in terms of  $\theta_2$ , putting  $p = 0$ .

The summation of all these processes, with appropriate sign,

<sup>1</sup> Smithells and Ransley, *loc. cit.*

gives the rate of diffusion  $D$  as a function of the pressure. The exact form of the equation depends upon the particular collision mechanisms which are considered effective, and here we cannot be quite certain. Smithells and Ransley found it possible to derive a basic equation of the form,

$$D = A\{\sqrt{1 + Kf(p)} - 1\},$$

where  $A$  and  $K$  are terms that include  $\theta$ . A simple form of this equation,

$$D = A\{\sqrt{1 + K\theta p} - 1\} . \quad . \quad . \quad (32)$$

can be made to agree very closely with the experimental results by selecting suitable values of  $a$  in the adsorption isotherm. The accuracy of this equation cannot be checked in the absence of exact knowledge of the extent of the adsorption under the conditions of the diffusion measurements. Adsorption measurements made with powders, and at lower temperatures, cannot be assumed to apply to sheet metal surfaces at higher temperatures, and at present exact data for such surfaces are not available.

It is interesting to note that equation (32) bears a close resemblance to the empirical equation (31) of Smithells and Ransley, and in particular that both equations approximate at high pressures to

$$D \propto \sqrt{p},$$

and at low pressures to

$$D \propto p.$$

Wang,<sup>1</sup> in the same way, has shown that by considering only the pairs of processes (1), (2), and (3) on page 104, the same conclusions are reached regarding the rate of diffusion at very high and very low pressures. This cannot be taken as proof that these three processes are alone effective, and further experimental data are necessary before the detailed mechanism of diffusion can be determined.

The general character of the diffusion process, however, is quite clear. There is no doubt that gases diffuse through metals in the atomic, and not in the molecular, state. This

<sup>1</sup> Wang, *Proc. Camb. Phil. Soc.*, 1936, **32**, 657.

conception, which appears to have originated with Ramsay,<sup>1</sup> is confirmed by all the experimental evidence. No other explanation of the  $\sqrt{p}$  law appears probable, and recent experiments with heavy hydrogen mixtures<sup>2</sup> give direct evidence of dissociation within the metal. This dissociation takes place when the gas molecule is adsorbed on the metal surface. At temperatures where diffusion can be measured, adsorption is of the activated type, and this almost certainly involves dissociation. The specific nature of diffusion is thus readily explained. Only those gases which undergo activated adsorption by a metal can diffuse through it. The rare gases are not adsorbed in this way by any metal, and attempts to measure their diffusion through various metals have always given negative results. Ryder<sup>3</sup> failed to detect any diffusion of argon through iron, and Baukloh and Kayser<sup>4</sup> found that nickel was impervious to helium, neon, argon or krypton. It is certain that if helium does diffuse through copper, nickel or molybdenum, the rate is at least  $10^5$  times slower than for the common gases.<sup>5</sup> Whilst nitrogen will diffuse through iron and molybdenum, it will not diffuse through copper. It is actively adsorbed by the first two metals, but is not adsorbed by copper above room temperature. Activated adsorption, with strong binding forces, is therefore a necessary preliminary to diffusion, and diffusion cannot occur as the result of purely physical adsorption. In a general way, it is possible to say whether diffusion will take place from a consideration of the chemical affinities of the gas and metal. Nitrogen will diffuse through metals which are capable of forming nitrides, like iron and molybdenum, but not through copper or silver towards which it is chemically inert. Carbon monoxide is a very stable molecule, and is not easily dissociated. It is almost certain that it will not diffuse through copper, but carbon and oxygen will diffuse through iron or nickel.

In passing, it should be noted that the diffusion of gases

<sup>1</sup> Ramsay, *Phil. Mag.*, 1894, 38, 206.

<sup>2</sup> Farcas and Farcas, *Proc. Roy. Soc.*, 1934, 144, 467.

<sup>3</sup> Ryder, *Elect. J.*, 1920, 17, 161.

<sup>4</sup> Baukloh and Kayser, *Z. Metallk.*, 1934, 26, 156.

<sup>5</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1935, 150, 172.



through glass and silica is of an entirely different character. The gas diffuses in the molecular state, diffusion is not specific, and the rare gases diffuse quite readily.<sup>1</sup> The process is a purely physical one, and no chemical forces are involved.

We may now consider the effect of a number of other factors on diffusion, and for convenience we will use the empirical equation

$$D = k\theta\sqrt{p},$$

which is sufficiently accurate for most purposes.

### Gas on Both Sides of the Metal.

So far we have discussed the diffusion of gas at a pressure  $p$  through a metal diaphragm into a vacuum. If instead of a vacuum the gas diffuses against a pressure  $p_1$  (where  $p_1 < p$ ) the equation becomes

$$D = k(\theta\sqrt{p} - \theta_1\sqrt{p_1}),$$

since the rate of diffusion depends on the difference in concentration of  $H^*$  just inside each surface.

### Diffusion of Mixed Gases.

Graham<sup>2</sup> observed in 1866 that when a palladium tube was surrounded by coal gas, only the hydrogen diffused through. This has actually been applied as a method of analysis, although it fails because the palladium soon becomes poisoned by the sulphur and hydrocarbons, and loses its diffusing power. If a diffusing gas is mixed with another gas which is not adsorbed at the temperature in question, the rate of diffusion is unaffected, and remains proportional to the partial pressure of the diffusing gas. Lombard<sup>3</sup> obtained the same values for the diffusion of hydrogen from nitrogen-hydrogen mixtures, as from purer hydrogen at the same partial pressures, within the limits of experimental error.

<sup>1</sup> Barrer, *J. Chem. Soc.*, 1934, 378.

<sup>2</sup> Graham, *Phil. Trans.*, 1866, 156, 399.

<sup>3</sup> Lombard, "Thesis," Paris, 1928.

The rate of diffusion of hydrogen at one atmosphere pressure is unchanged when the total pressure is increased to 120 atmospheres by the addition of nitrogen.

This principle provides a very convenient means of introducing small quantities of pure gases into vacuum apparatus for experimental purposes. A palladium tube attached to the apparatus is heated whilst surrounded by a reducing gas flame, or a stream of hydrogen, and pure hydrogen only diffuses through into the apparatus. A silver tube may be used in the same way to introduce oxygen from the air.

When both gases in a mixture are capable of diffusing, the position is more complicated. In this case we have the two equations

$$D_1 = k_1 \theta_1 \sqrt{p_1}; \quad D_2 = k_2 \theta_2 \sqrt{p_2},$$

where the suffixes apply to the two gases respectively. The values of  $\theta_1$ ,  $\theta_2$  are given by the appropriate isotherms for two competing gases.<sup>1</sup> If one is much more strongly adsorbed than the other, it will diffuse more rapidly than would be expected simply on the basis of partial pressure. It may happen that the more strongly adsorbed gas diffuses very slowly, if at all, and this leads to poisoning, of which we have just had an example in the case of coal gas and palladium. This phenomenon is discussed more fully later.

An interesting example of two gases whose adsorptive and diffusing powers are not widely different, is provided by the isotopes of hydrogen. The relative rates of diffusion of these two gases have been studied by a number of workers. The ratio of their thermal velocities at any temperature is  $1 : \sqrt{2}$ , and, as would be expected, their diffusivities have very closely the same ratio. Jouan<sup>2</sup> found the rates of diffusion of hydrogen and deuterium through platinum at 450°-950° C. to be in the ratio of 1 to 1.33, and Jost and Widmann<sup>3</sup> for palladium at 300° C. found 1 to 1.35. Melville and Rideal<sup>4</sup> found values

<sup>1</sup> See p. 8.

<sup>2</sup> Jouan, *Z. Phys. Radium*, 1936, 7, 101.

<sup>3</sup> Jost and Widmann, *Z. Phys. Chem.*, 1935, 29, 247.

<sup>4</sup> Melville and Rideal, *Proc. Roy. Soc.*, 1935, 153, 77, 89.

between 1.5 and 1.80 for platinum, nickel and copper at 225°-362° C. The temperature coefficient is different for the two gases, the difference in activation energy being about 600 calories, which agrees with the difference in activation energies found for these gases in catalytic reactions at metal surfaces.

### Diffusion through Composite Metal Sheets.

We have seen that the rate of diffusion is inversely proportional to the thickness of the metal. If two sheets of metal 1 mm. thick are clamped together, the rate of diffusion is the same as that for a single sheet 2 mm. in thickness.<sup>1</sup> In the case of two different metals the resistance to diffusion must also be additive, but if one is much more permeable than the other, the rate will be determined almost entirely by the one that offers the most resistance. Thus Melville and Rideal<sup>2</sup> found that palladium could be used as an inert support for electrodeposited layers of copper. The rate through a diaphragm of copper on palladium was unchanged when the copper was covered with palladium, to give a Pd—Cu—Pd membrane. A plate consisting of Cu—Pd—Cu gave half the rate of a plate consisting of Cu—Pd, the thickness of the copper being the same in each layer.

Ham<sup>3</sup> found that a double layer of palladium and nickel behaved exactly like the same thickness of nickel alone. On the other hand, he obtained a surprising result with double layers of platinum and nickel, which have about the same permeability, for he found that the value of the exponential  $E_0$  was determined entirely by the outgoing surface. In other words, the temperature coefficient was that of nickel when the gas passed from platinum to nickel, but that of platinum when the direction of diffusion was reversed.

From the results obtained with palladium the interesting fact emerges that it makes no difference whether the surface

<sup>1</sup> Lombard, *loc. cit.*

<sup>2</sup> *Loc. cit.*

<sup>3</sup> Ham, *Phys. Rev.*, 1934, 45, 741; *J. Phys. Chem.*, 1933, 1, 476.





FIG. 74.—Section through wall of nickel tube after oxygen diffusion at  $900^{\circ}$  C. showing oxygen rich layer at the surface, indicated by the arrows.  $\times 200$ .

*[To face page 111.*

is supplied with molecules from the gas phase, or with atoms from the palladium. The possible explanation is that the atoms recombine at the interface, and are again dissociated on entering the second metal layer.

### Influence of the State of the Surface.

Smithells and Ransley<sup>1</sup> have shown that the rate of diffusion may become independent of the gas pressure if a compound between the gas and the metal is formed on the surface. The diffusion of oxygen through nickel at 900° C. becomes independent of pressure at about 0.25 mm. Above this pressure a layer of nickel oxide is visible on the surface. Fig. 74 shows a section through the wall of a tube that has been used for diffusion measurements. It will be seen that a zone rich in nickel oxide has formed to a depth of about  $2 \times 10^{-3}$  cm. below the surface of the metal. At 900° C. nickel dissolves about 1.1 per cent. NiO. The depth of this zone increases steadily because the rate of passage of oxygen through the surface is faster than the rate of diffusion through the metal. The rate of diffusion is simply determined by the difference in the oxygen concentration in this zone and at the inner surface of the tube, where it is substantially zero. Oxygen is supplied to the nickel from the oxide layer at a rate which is independent of the gas pressure. The gas pressure may influence the rate of oxidation (although even this is doubtful),<sup>2</sup> but cannot influence the rate of diffusion. This explanation of the constancy of the rate of diffusion at pressures above the critical value of 0.25 mm. is independent of any assumptions regarding the nature of the reactions taking place at the gas-metal interface. At lower pressures, when no oxide is formed on the surface, we may assume that the rate of penetration through the surface is the limiting factor, and that diffusion in the metal is comparatively rapid. In this range of pressure the rate of diffusion appears to be roughly proportional to  $\sqrt{p}$ , as seen in

<sup>1</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1936, 157, 292.

<sup>2</sup> See Wilkins, *ibid.*, 1930, 128, 407.

Fig. 75, and is therefore similar to the diffusion of hydrogen, where no compound is formed.

Since adsorption is a controlling factor in diffusion, it is clear that any change in the state of the surface, such as activation or poisoning, which affects its adsorptive power, will also affect the rate of diffusion. The specific surface of an adsorbent is usually from 1 to 20 times its measured surface, and can by suitable treatment be increased some hundredfold. Roughening the surface either mechanically, by etching, or by alternate oxidation and reduction, not only increases the area available for adsorption, but also the proportion of the surface which is active. Such treatments increase the value of the adsorption coefficient  $\alpha$  and, therefore, the rate of diffusion at low pressures. Some experimental data<sup>1</sup> for the effect of surface treatment on the diffusion of hydrogen through iron and nickel are given in Table 10. In the case of iron, etching the surface with dilute

TABLE 10.  
EFFECT OF SURFACE TREATMENT ON RATE OF DIFFUSION.

Metal.	Treatment.	Temp. °C.	Pressure, mm.	Rate D.
Nickel	Polished . . . .	750	0.042	$1.39 \times 10^{-6}$
	Oxidised and reduced . .	750	0.042	2.70
	Polished . . . .	750	0.091	2.91
	Oxidised and reduced . .	750	0.091	4.23
Iron	Polished . . . .	400	0.77	$0.47 \times 10^{-7}$
	Etched . . . .	400	0.77	4.4
	Polished . . . .	590	0.073	1.28
	Oxidised and reduced at 600° C.	590	0.073	0.76
	Further reduced at 800° C. .	590	0.073	1.54

nitric acid has increased the rate of diffusion ten times. In Fig. 76 the rate of diffusion of hydrogen through iron tubes with etched and polished surfaces is plotted against  $\sqrt{p}$ . The effect of adsorption is shown by the much higher rate of

<sup>1</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1935, 150, 172.

diffusion for the etched surface at low pressures, the surface of the polished tube being then incompletely covered. The rate of diffusion of hydrogen through iron may be increased 10 or

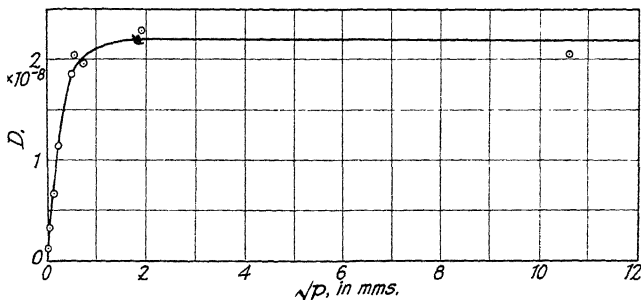


FIG. 75.—Effect of pressure on diffusion of oxygen through nickel at 900° C.

15 times by heating the metal in nitrogen,<sup>1</sup> although the normal rate is recovered by prolonged treatment in vacuo. The reverse effect is produced when the surface is poisoned by a substance that is more strongly adsorbed than the gas in question. If the metal is slightly oxidised, for example, the rate of diffusion is usually much reduced. Observed changes in the rate of diffusion with a given sample are generally to be ascribed to changes in the structure of the surface, or to substances adsorbed

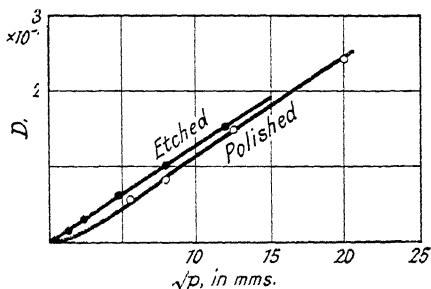


FIG. 76.—Effect of surface treatment on rate of diffusion. Hydrogen—iron at 726° C.

thereon. Palladium appears to be particularly affected by preliminary treatment, and its capricious behaviour has been noted by a number of workers.<sup>2, 3, 4, 5</sup> The permeability generally

<sup>1</sup> Ham, *Phys. Rev.*, 1935, 47, 337.

<sup>2</sup> Ham, *ibid.*, 1934, 45, 741.

<sup>3</sup> Lombard, Eichner and Albert, *C. Rend.*, 1936, 202, 1777.

<sup>4</sup> Lombard and Eichner, *Bull. Soc. Chim.*, 1933, 53, 1176.

<sup>5</sup> Smith and Derge, *Trans. Electrochem. Soc.*, 1934, 66, 253; *J. Amer. Chem. Soc.*, 1934, 56, 2513.



falls if hydrogen is allowed to diffuse for some time at temperatures above  $500^{\circ}\text{C}$ ., although this effect varies very much with different specimens. Pure palladium seems to be less affected than metal containing impurity.<sup>1, 2</sup> Ham<sup>3</sup> found that the rate of diffusion for fresh massive palladium fell to  $1/50$  of its original value after several hours at  $1000^{\circ}\text{C}$ . The permeability may be recovered by heating at  $500^{\circ}\text{C}$ . in oxygen, which results in a film of oxide being formed on the surface, followed by reduction in hydrogen at  $150^{\circ}\text{C}$ . Heating in nitrogen increases the permeability of palladium. Whilst many of these effects must be attributed to changes in the state of the surface, palladium is somewhat exceptional, since it shows a very marked expansion when heated in hydrogen, and ultimately becomes disintegrated.

Baukloh and Kayser<sup>4</sup> observed that the rate of diffusion of hydrogen through nickel remained fairly constant up to  $850^{\circ}\text{C}$ ., but that at higher temperatures it gradually fell off. At  $1060^{\circ}\text{C}$ . the rate fell to 30 per cent. of its initial value after 6 hours.

Aluminium is only very slightly permeable to hydrogen, and the rate of diffusion is difficult to determine, since it is very sensitive to traces of oxygen adsorbed on the surface. Smithells and Ransley<sup>5</sup> were able to study this with an arrangement that enabled both the inside and outside surfaces of the diffusion tube to be scraped mechanically *in vacuo*, or during the course of diffusion. When aluminium is exposed to the air a transparent but protective film of oxide forms on the surface, and a diffusion tube is naturally in this state when introduced into the diffusion apparatus. If this oxide film is removed by mechanical abrasion *in situ* the rate of diffusion is immediately increased about ten-fold. In spite of the utmost precautions to avoid the presence of water vapour or other oxidising gases, this high rate of diffusion gradually decays, and after 4 or 5 hours falls to the original value for the exposed tube. If the rate of diffusion is plotted against the time, curves are obtained similar

<sup>1</sup> Lombard, Eichner and Albert, *C. Rend.*, 1936, **202**, 1777.

<sup>2</sup> Lombard and Eichner, *Bull. Soc. Chim.*, 1935, **2**, 1555.

<sup>3</sup> Ham, *Phys. Rev.*, 1934, **45**, 741.

<sup>4</sup> Baukloh and Kayser, *Z. Metallk.*, 1934, **26**, 156.

<sup>5</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1935, **152**, 706.

to those shown in Fig. 77. The final rate in each run is the same as that found for a tube which had been deliberately oxidised by anodic treatment, and indicates that the decay is almost certainly due to oxygen poisoning of the surface. The rate of diffusion for a poisoned surface is so low at temperatures more than  $100^{\circ}\text{C.}$  below the melting-point of the metal as to

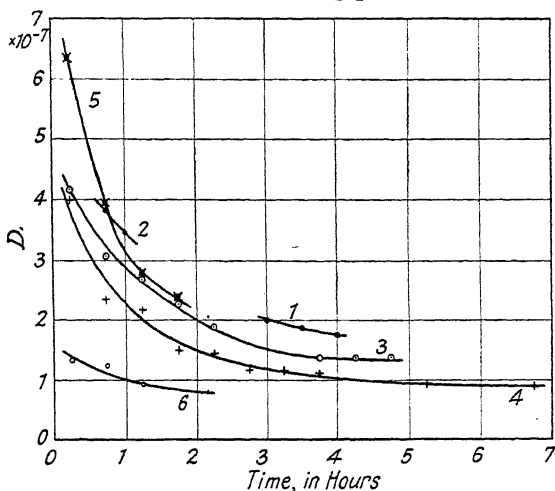


FIG. 77.—Effect of surface treatment on diffusion of hydrogen through aluminium.

Run 1	Exposed to air.
„ 2	Outer surface scratched.
„ 3	„ „ „ again.
„ 4	„ „ „ „
„ 5	Inner and outer surfaces scratched.
„ 6	Outside anodically oxidised.

be almost unmeasurable, and accounts for the frequent failure to detect diffusion of hydrogen through aluminium.<sup>1</sup>

In all diffusion measurements it is important to work with clean surfaces and pure gases. It is generally desirable to allow diffusion to proceed for some time at a temperature considerably higher than that at which measurements are subsequently to be made. This not only aids in the removal

<sup>1</sup> Deming and Hendricks, *J. Amer. Chem. Soc.*, 1923, 45, 2857; Baukloh and Kayser, *Z. Metallk.*, 1935, 27, 281.

of adsorbed impurities, but as the result of recrystallisation and evaporation produces a structure at the surface of the metal which will remain stable at lower temperatures.

### The Effect of Structure.

In considering the mechanism of the diffusion process it is important to examine the evidence regarding the effect of the grain size of the metal and other factors relating to the internal structure. Different views have been expressed as to whether diffusion takes place wholly or partly through

- (a) grain boundaries,
- (b) cleavage planes,
- (c) the crystal lattice,

and the evidence is by no means conclusive.

At first sight, a grain boundary would appear to offer an easier path for gas to pass through a metal than any other. It is generally assumed that at a grain boundary the atomic spacing is rather greater than it is in the orderly arrangement within the crystal. It often happens that the action of a gas results in a visible change taking place at the grain boundaries, when the crystals themselves remain unchanged under the microscope. When copper is heated in hydrogen it becomes brittle, due to the reduction of the cuprous oxide particles. The microscope reveals a widening of the grain boundaries which accounts for the intercrystalline weakness. This does not prove, however, that the hydrogen entered in this way, and the cracks may be entirely due to pressure exerted by the water vapour resulting from the reduction, the grain boundaries, which are the weakest part of the metal at elevated temperatures, being the first to give way.

A similar effect is produced when mild steel is heated for long periods in ammonia, and intercrystalline fissures such as those seen in Fig. 78 eventually destroy the material. These again are probably due to the action of the reducing gases on the carbon and other constituents in the steel. Case-hardened steel shows the excess of carbide in the grain boundaries and cleavage planes, as seen in Fig. 79. This again is not evidence



FIG. 78.—Surface of mild steel tube after heating at  $300^{\circ}$ - $600^{\circ}$  C. in ammonia.  $\times 8$ .

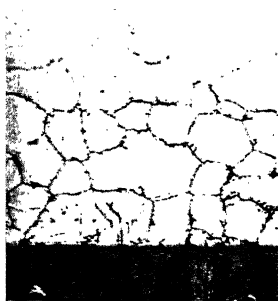


FIG. 79.—5 per cent. Ni steel after cementation. Etched sodium picrate.  $\times 100$ .

*[To face page 116.]*



of gases penetrating down the grain boundaries, but results from the precipitation of carbide originally held in solution. The oxidation of certain metals appears to proceed definitely down the grain boundaries, a good example of this effect in a nickel-chromium alloy being shown in Fig. 80. This may be due to penetration of oxygen more rapidly down the grain boundaries, or it may be analagous to the oxidation of copper at low temperatures as investigated by Wilkins.<sup>1</sup> Whilst at high temperatures the oxygen definitely passes through the lattice of the cuprous oxide layer, and so attacks the underlying metal, below 600° C. the oxygen can only pass down the boundaries between the oxide crystals. Their size depends on the grain size of the original copper, and the adsorbed oxygen atoms must migrate over the surface until they can pass down a grain boundary. If adsorption follows the Langmuir isotherm the surface will become saturated at a certain pressure, and further increase in pressure should not, therefore, result in increased oxidation. This point is of importance, for the same effect should be found in all cases where diffusion is confined to the grain boundaries. As we have seen, however, an increase in pressure always results in an increased rate of diffusion, except when a distinct phase, such as an oxide, is formed on the surface.

The effect of gases on the mechanical properties of metals is of some importance in this connection. Whilst the hardness of electrodeposited metals was at one time attributed to the presence of occluded hydrogen, it is now clear that this is due to the indirect effect of the gas in refining the grain size rather than to its actual presence in the metal (see p. 196). On the other hand, the brittleness induced in steel, and some other alloys, by pickling, appears to be the direct effect of hydrogen in the metal. Pfeil has shown<sup>2</sup> by experiments with large crystals of iron that pickling weakens the grain boundaries and reduces the cohesion on the cleavage planes, indicating that the passage of hydrogen may have been mainly at these points. If palladium is allowed to cool in hydrogen, and is then polished

<sup>1</sup> Wilkins, *Proc. Roy. Soc.*, 1930, 128, 407.

<sup>2</sup> Pfeil, *ibid.*, 1926, 112, 182.

and etched, a number of lines or sub-boundaries appear, as shown in Fig. 81, which are not normally present in the micro-structure. Smith and Derge<sup>1</sup> have identified these lines as traces of certain (110) and (111) planes which cut the surface. They conclude that the penetration of hydrogen takes place preferentially along these cleavage planes, the subsequent diffusion into the lattice being a much slower process.

The diffusion of one metal into another obeys the same kind of law as for gaseous diffusion, and the effect of temperature is represented by the equation

$$D = A \cdot e^{-\frac{b}{RT}}.$$

In certain cases of intermetallic diffusion there is clear evidence that the grain boundaries play an important part. The diffusion of thorium in tungsten has probably been more thoroughly investigated than any other case, owing to its industrial importance in the production of thermionic cathodes for valves. The emission from these cathodes depends on the formation of an adsorbed film of thorium atoms on the surface of a tungsten wire. The thorium is produced in the body of the wire by the reducing action of the tungsten on thorium oxide incorporated with it. This takes place at 2500° C., and on subsequently maintaining the filament at 1800° C. the thorium slowly diffuses to the surface. If the tungsten has a small grain size it is easy to maintain a fairly complete monatomic layer of thorium on the surface, but if the wire consists of large crystals the rate of arrival is insufficient to compete with the rate of evaporation, and much lower values of thermionic emission are obtained. Clausen<sup>2</sup> has shown that if a thoriated wire is covered with a layer of pure tungsten in the form of a single crystal, the rate of diffusion of thorium to the surface is so slow that practically no emission is obtained. The ratio of emission from a Pintsch single crystal wire to that from an ordinary fine grained wire, was found to be about 1 to 100,000. The effect of grain size on the rate of diffusion

<sup>1</sup> Smith and Derge, *Trans. Electrochem. Soc.*, 1934, 66, 253; *J. Amer. Chem. Soc.*, 1934, 56, 2513.

<sup>2</sup> Clausen, *Physica*, 1927, 7, 193.

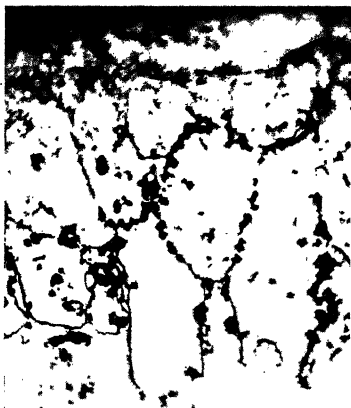


FIG. 80.—80/20 nickel chromium alloy heated for  $3\frac{1}{2}$  hours at  $1250^{\circ}$  C. in air, showing oxide penetration along grain boundaries. Unetched.  $\times 100$ .

[See page 117.



FIG. 81.—Rolled palladium foil saturated with hydrogen electrolytically, etched chromic-nitric acid.  $\times 150$ .

[Smith and Derge.

[To face page 118.





of thorium in tungsten has also been studied by Fonda.<sup>1</sup> He obtained normal activation rates for single crystal wire after plastic deformation, presumably due to the development of faults in the lattice through which diffusion could proceed. The conclusion to be drawn from these results is that the thorium diffuses extremely slowly through the lattice of the tungsten until it reaches a grain boundary, along which it travels at a much higher rate to the surface.<sup>2</sup> On the other hand, Benjamin<sup>3</sup> has been unable to detect by the electron microscope any evidence for grain boundary diffusion of barium in nickel under exactly similar conditions. The data on inter-metallic diffusion for other systems has been summarised in several papers by Seith.<sup>4</sup> The diffusion of one metal into another most probably depends on atoms changing places in the lattice, whereas we shall see that this is probably not the mechanism in gas diffusion, and grain boundaries may not, therefore, have the same significance.

If the grain boundaries play any important part in diffusion we should expect to find that the rate of diffusion depended on the grain size of the metal. No confirmation of this is given by such experimental data as are available. Baukloh and Kayser<sup>5</sup> were unable to detect any difference in the rate of diffusion of hydrogen through samples of nickel of different grain size. Edwards<sup>6</sup> measured the rate of diffusion of hydrogen through a single crystal of iron  $1\frac{1}{2}$  inches in diameter and  $1/16$ -inch thick and again after heating it above the A<sub>3</sub> point to refine the grain. The rate of diffusion was the same in both states. Smithells and Ransley repeated this experiment with an iron tube which was converted into a single crystal by Pfeil's method. The rates of diffusion given below are seen to be identical with those for a similar tube having 100 grains per square mm.

<sup>1</sup> Fonda, Young and Walker, *Physics*, 1933, 4, 1.

<sup>2</sup> Langmuir, *Franklin J.*, 1934, 217, 543.

<sup>3</sup> Dr. M. Benjamin, Res. Labs., G.E.C. Ltd., Wembley (unpublished).

<sup>4</sup> Seith and Keil, *Z. Metallk.*, 1933, 25, 104; 1935, 27, 213; v. Hevesy and Seith, *Metallwirtschaft*, 1934, 13, 479.

<sup>5</sup> Baukloh and Kayser, *Z. met.*, 1934, 26, 156.

<sup>6</sup> Edwards, *J. Iron Steel Inst.*, 1924, 110, 9.

It must therefore be concluded that, at any rate in the case of hydrogen and iron, diffusion is a lattice process, and the grain boundaries play no part.

EFFECT OF GRAIN SIZE ON RATE OF DIFFUSION  
OF HYDROGEN THROUGH IRON

Temperature, °C.	Pressure, mm.	Rate D.	
		Fine Grain.	Single Crystal.
245	140	$2.4 \times 10^{-6}$	$1.2 \times 10^{-6}$
413	140	17.6	17.1
621	140	92.8	89.5
779	140	203.0	205.0

As we have seen, however, it is possible that in other cases the grain boundaries or the cleavage planes may offer an easier path for the gas to enter the metal, and further experimental work is still required in this field.

The existing data can be interpreted satisfactorily on the assumption that lattice diffusion is normal for gas-metal systems, although grain boundaries and lattice imperfections may provide active centres for adsorption and facilitate the entry of the gas. Even though the metal has a close-packed lattice, it is not difficult to conceive of a gas atom penetrating the lattice. We have postulated that for diffusion to take place there must be a strong binding force between the gas atom and the metal atom at the surface, and this must also be true inside the metal. The presence of a foreign atom will cause a distortion of the lattice. If the binding force between the gas atom and the metal atom to which it is momentarily attached is large, the metal atom will be less firmly bound to its neighbours, resulting in a distortion which will facilitate the passage of the gas atom. This is illustrated in Fig. 82.

Diffusion results from the successive formation of unstable gas-metal associations, the gas atom being handed on from one metal atom to another, the rate and direction of diffusion being determined by the concentration at different points in

the metal. The experiments of Seith on the diffusion of other metals into solid lead, have shown that the rate of diffusion is more rapid the more the outer electron shell of the foreign atom differs from that of lead. The diffusion of radioactive lead into ordinary lead is the slowest of all. This indicates that the distortion of the lattice, resulting from the chemical affinity of the diffusing atom and the metal, is an essential factor in the diffusion process.

Any alteration produced in the crystal lattice of the metal may, therefore, be expected to affect diffusion. Changes in the rate of diffusion at the transition temperature have been observed in metals which undergo magnetic transformations.<sup>1</sup> Discontinuities are found in the isobars for pure nickel at 360° C. corresponding to the Curie point, and for pure iron at 760° C. Palladium-nickel alloys also show the discontinuity at 360° C.

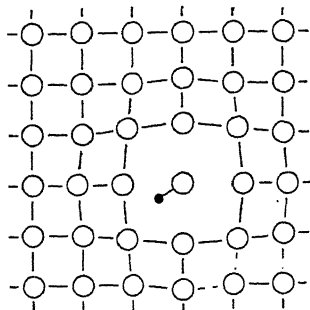


FIG. 82.

### The Effect of Impurities.

Foreign atoms, present either as impurities or as alloying constituents in the metal, may be expected to have some effect on the ease with which the gas atoms can penetrate into the lattice. This appears to be so, but practically no quantitative measurements have been made on the effect of composition on diffusivity. Lombard and Eichner found that the rate of diffusion of hydrogen through palladium increased with the purity of the metal, the value for commercial palladium being about 60 per cent. of that for the purest metal obtainable. The impurities were not stated.

Baukloh<sup>2</sup> has obtained somewhat conflicting results on the

<sup>1</sup> Ham, *Phys. Rev.*, 1936, 49, 195; *Amer. Soc. Metals*, Preprint, Oct., 1936; Baukloh and Kayser, *Z. Metallk.*, 1935, 27, 281.

<sup>2</sup> Baukloh and Guthmann, *ibid.*, 1936, 28, 34; Lewkonja and Baukloh, *ibid.*, 1933, 25, 309.

effect of the carbon content on the diffusion of hydrogen through steel. Below  $700^{\circ}\text{C}$ . the rate of diffusion decreased with increase in carbon content. Above the  $\alpha$ - $\gamma$  transition temperature the high carbon steels appeared to be more permeable, confirming the results obtained by Thanheiser.<sup>1</sup> The addition of chromium to steel containing 0.1-0.2 per cent. C also reduced the rate of diffusion at  $700^{\circ}\text{C}$ .

A most thorough investigation of the effect of composition on the diffusion of the various constituents of steel has been

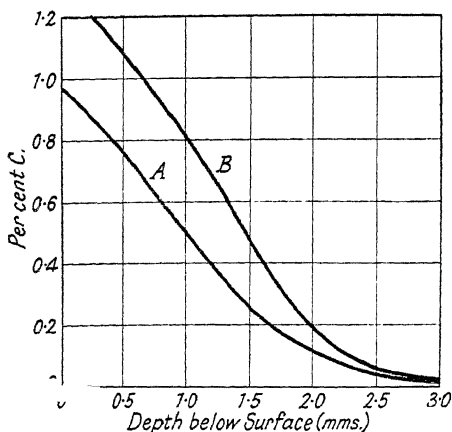


FIG. 83.—Effect of dissolved oxygen on the diffusion of carbon into steel.

A. Armco iron carbonised 10 hours at  $1000^{\circ}\text{C}$ . in  $\text{CO}$ .

B. Armco iron heated 100 hours at  $1000^{\circ}\text{C}$ . in dry hydrogen and then carbonised as A.

carried out by Bramley<sup>2</sup> and his collaborators. Whilst much of this work refers to the non-metallic elements in steel, and not strictly to gases, the results have an important bearing on the problem of diffusion. Diffusion was studied by heating steel bars, about 25 cm. long and 3 cm. in diameter, in various

<sup>1</sup> Thanheiser, *Z. tech. Phys.*, 1929, 10, 143.

<sup>2</sup> Bramley and Jinkings, *Carnegie Schol. Mem.*; *Iron. Steel Inst.*, 1926, 15, 17 and 127; Bramley and Beeby, *ibid.*, p. 71; Bramley, *ibid.*, p. 155; Bramley and Lawton, *ibid.*, 1927, 16, 35; Bramley and Heywood, *ibid.*, 1928, 17, 67; Bramley and Lord, *ibid.*, 1929, 18, 1; Bramley, Heywood, Cooper and Watts, *Trans. Faraday Soc.*, 1935, 31, 707.

gases, and determining the depth of penetration by analysis of successive layers turned off in the lathe. The kind of result obtained is shown by the curves given as examples in Figs. 83 and 84. The concentration of the diffusing element (C, N, S, etc.) at various depths below the surface was found to conform to Fick's linear diffusion law,<sup>1</sup> by means of which the diffusivity constant could be calculated in each case. It was also established that the diffusivity constant  $\Delta$  varied with the temperature according to the usual logarithmic relation

$$\log \Delta = k \cdot \frac{1}{T}.$$

The most important results of this work may be summarised as follows :

When pure iron is heated above 850° C. in carbon monoxide, carbon diffuses into the metal. The diffusivity constant is independent of the carbon content, but the rate of diffusion decreases as the carbon content of the steel is increased. This is simply due to the resultant decrease in the carbon concentration gradient between the surface and the centre of the bar, and with a sufficiently high carbon content (e.g. 1.54 per cent. C at 950° C.) no penetration takes place. Slightly different values for the diffusivity constant  $\Delta$  are obtained with other carbonaceous gases, as seen in Table 11 (p. 124).

The presence of sulphur, phosphorus or oxygen in the steel obstructs the diffusion of carbon. This is shown by the lower values of  $\Delta$ , which implies that a greater difference in concentration is required to maintain a given rate of diffusion. With methyl cyanide both carbon and nitrogen diffuse independently of each other.

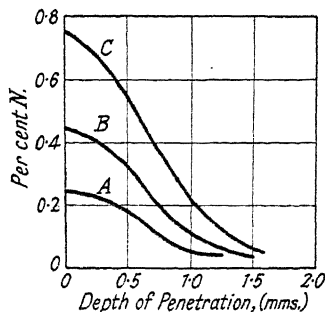


FIG. 84.—Effect of dissolved oxygen on diffusion of nitrogen in iron. Before nitriding in ammonia samples were treated thus :

- A. Swedish iron untreated ;
- B. Oxidised for 30 hours at 1100° C. in 75 per cent. CO, 25 per cent. CO<sub>2</sub> ;
- C. Oxidised for 100 hours in a malleablising furnace.

<sup>1</sup> See p. 86.

When steel is heated in ammonia, nitrogen diffuses into the metal. Diffusion of nitrogen is obstructed by the presence of carbon, but dissolved oxygen increases the diffusivity. If, however, the surface of the steel is oxidised, nitriding is completely suppressed, since the nitrogen is no longer adsorbed on the surface.

The diffusion of sulphur, phosphorus and oxygen into steel was studied by heating in mixtures of  $H_2 + H_2S$ ,  $H_2 + PH_3$

TABLE 11.  
DIFFUSIVITY CONSTANTS AT  $1000^\circ C$ .

Metal.	Gas.	Diffusing Element.	$D_{1000^\circ C}$ .
Armco iron . . . .	CO	C	$20 \times 10^{-8}$
	CO + petrol	C	$21.5 \times 10^{-8}$
	CO + xylene	C	$12.0 \times 10^{-8}$
Armco iron containing S	CO	C	$7.5 \times 10^{-8}$
" " " O	CO	C	$14.0 \times 10^{-8}$
" " " P	CO	C	$10.0 \times 10^{-8}$
Armco iron . . . .	$H_2 + H_2S$	S	$5.5 \times 10^{-10}$
" " " . . . .	CO + $CO_2$	O	$1 \times 10^{-10}$
Steel 0.03 per cent. C .	$H_2 + PH_3$	P	$16 \times 10^{-10}$
" 0.15 " " .	$H_2 + PH_3$	P	$7 \times 10^{-10}$
" 0.96 " " .	$H_2 + PH_3$	P	$1.3 \times 10^{-10}$
Armco iron . . . .	$H_2 + NH_3$	N	$1.8 \times 10^{-10}$

and  $CO + CO_2$  respectively. The diffusion of each of these elements is retarded by the presence of carbon in the steel, and becomes slower as the carbon content is increased.

Thus we see that the diffusion of each of these elements is influenced by the presence of the others. The explanation probably lies in the effect produced on the lattice of the iron crystals through which they have to travel.

Practically no information is available regarding the effect of composition on the permeability of the simple binary alloys. In a few cases the effect on solubility has been determined, and since the rate of diffusion is related to the solubility, some

general conclusions may be drawn from this work. The only direct measurements that appear to have been made are those of Baukloh and Kayser<sup>1</sup> for the diffusion of hydrogen through nickel-copper and nickel-iron alloys. Some of their results

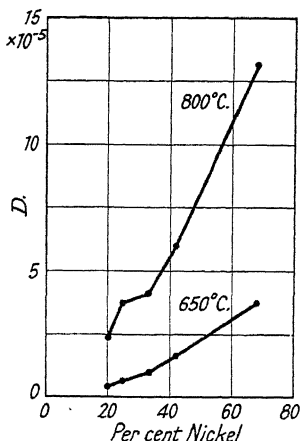


FIG. 85.—Nickel-copper alloys. Effect of composition on rate of diffusion of hydrogen at 760 mm.

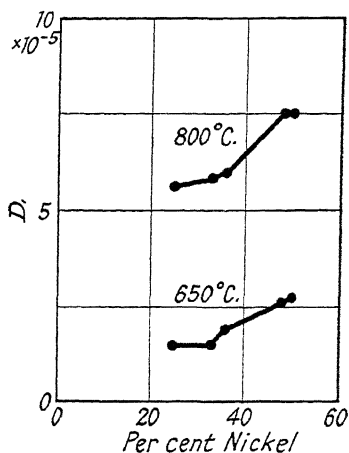


FIG. 86.—Nickel-iron alloys. Effect of composition on rate of diffusion of hydrogen at 760 mm.

[Baukloh and Kayser.

are shown in Figs. 85 and 86. In both cases the rate of diffusion increases with increase in the nickel content. It appears that the nickel confers its high permeability on the alloys, the effect being most marked in the case of copper, which is itself very impermeable to hydrogen.

### Imperfections in Crystals.

It is now very generally believed that the individual crystals in a metal are not perfect, but that they have some kind of secondary structure, although there is a divergence of opinion as to its precise nature. If such structures exist they may well be expected to affect both adsorption on the surface and diffusion in the interior of metal crystals, and a brief account

<sup>1</sup> Baukloh and Kayser, *Z. Metallk.*, 1935, 27, 281.



of the evidence for their existence may be given.<sup>1</sup> A theoretical consideration of the structure of crystals led Lennard-Jones<sup>2</sup> to the conclusion that, owing to the unbalanced atomic forces, the distance between the atoms at the surface of a salt crystal should be about 5 per cent. less than the normal atomic spacing in the lattice, whilst in a metal crystal the distance would be rather greater than the normal. This idea was developed by Smekal<sup>3</sup> and later by Zwicky,<sup>4</sup> in an attempt to account for the discrepancy between the actual and theoretical strength of metal crystals.

Zwicky assumed that planes having an abnormal spacing could also exist within the crystal and that as a result the crystal was broken up into a block, or mosaic, structure. The theoretical basis for this assumption now appears to be unsound, but there are a number of independent observations which are most readily explained by a hypothesis of this kind.

It is very commonly observed that large crystals when deeply etched do not show a smooth surface, but either a series of steps or etch pits having dimensions of some 1000 or 100 atom diameters,<sup>5</sup> that is from  $10^{-4}$  to  $10^{-6}$  cm. Cleavage planes<sup>6</sup> also very often show a series of parallel lines having a spacing of about this order. The spacing between slip planes is again very similar, the value found by Andrade and Hutchings<sup>7</sup> for pure mercury being  $5 \times 10^{-3}$  cm. These observations are supported both by electron and X-ray diffraction patterns.<sup>8</sup> Whereas a perfect crystal should only give reflection at the angle required by Bragg's law, it is usually found that reflection is obtained over an angle that varies from a few minutes to a few degrees of arc. The fact that the

<sup>1</sup> For a more complete account see Hume-Rothery, "The Structure of Metals and Alloys," Inst. of Metals Monograph, 1936; also Goetz, *Int. Conf. Physics*, 1934, 2, 62.

<sup>2</sup> Lennard-Jones, *Proc. Roy. Soc.*, 1924, 106, 441, 463, 709; Lennard-Jones and Dent, 1928, 121, 247.

<sup>3</sup> Smekal, *Phys. Zeit.*, 1925, 26, 707; *Z. Physik*, 1929, 55, 289.

<sup>4</sup> Zwicky, *Proc. Nat. Acad. Sci.*, 1929, 15, 816.

<sup>5</sup> G. I. Taylor, *Proc. Roy. Soc.*, 1934, 145, 362, 388, 405.

<sup>6</sup> Goetz, *Proc. Nat. Acad. Sci.*, 1930, 16, 99; *Phys. Rev.*, 1934, 45, 138.

<sup>7</sup> Andrade and Hutchings, *Proc. Roy. Soc.*, 1934, 148, 120.

<sup>8</sup> Thomson, *Phil. Mag.*, 1934, 18, 640.

reflections are sharp implies that the effect is not due to a general distortion of the whole lattice. These results are most readily explained by assuming that the crystal is composed of fragments having slightly different orientations. The size of the fragments as judged both from the electron and X-ray patterns again appears to be about  $10^{-4}$  cm. James<sup>1</sup> found with aluminium, for example, that the mosaic structure was developed by mechanical deformation, and tended to disappear on annealing. Similar effects are obtained when metal vapours are condensed on a cold surface, and the crystals frequently develop a stepped or laminated structure, consisting of plates about  $10^{-3}$  to  $10^{-4}$  cm. thick.<sup>2</sup>

Whilst there is, perhaps, no direct evidence of the existence of a mosaic structure, these and similar observations all point in the same direction. What part these discontinuities play in gas-metal equilibria is still more a matter of speculation. It is possible that the gaps between the blocks correspond to the planes by which, according to Smith and Derge, hydrogen enters most readily into palladium. If they exist, they might well be expected to aid diffusion. The edges and corners of the blocks have, by others, been identified with the active centres of metal catalysts. Until more precise knowledge is available we can only bear in mind that metal crystals may not have the simple structure previously attributed to them.

### Diffusion of Nascent Hydrogen.

Reference has already been made to the fact that hydrogen produced by a chemical or electrochemical reaction at the surface of a metal is not all evolved as gas, but that some of it may diffuse into the metal. This is of very great practical importance in many cases, because the properties of the metal may be profoundly modified by the gas, as evidenced, for example, by the brittleness of steel which has been pickled in acid, and the hardness of electrodeposited metals. In spite of the practical importance of this aspect of diffusion it has

<sup>1</sup> James, *Z. Krist.*, 1934, 89, 306.

<sup>2</sup> Straumanis, *Z. Phys. Chem.*, 1931, 13, 316; 1932, 19, 63.

received rather scant attention, and experimental work has been almost entirely confined to iron and steel. Hydrogen will diffuse into palladium under similar conditions, but whilst this method is commonly used for saturating the metal with gas and for solubility determinations, no quantitative measurements of diffusion have been made. Charpy and Bonnerot<sup>1</sup> were unable to detect any diffusion through copper when it was made the cathode in an electrolytic bath, and observations are lacking on other metals. Indirect evidence that hydrogen may enter aluminium during pickling under certain conditions has been obtained.<sup>2</sup>

Diffusion only occurs if the hydrogen is actually liberated at the surface of the metal. If a second sheet of metal is placed close to the actual cathode, the gas does not diffuse through it, showing that only the hydrogen ions can diffuse and not the molecular gas liberated as bubbles. We may first consider experiments in which the hydrogen is produced by electrochemical action. In measurements of this kind a considerable period elapses before the conditions become steady. Not only has the metal to become saturated, but changes in the conditions at the surface due to the action of electrolysis affect the course of diffusion, and must be allowed to reach equilibrium. It is better if possible to use dilute solutions of alkalis, rather than acid solutions which corrode the surface more rapidly. The phenomena of electrolytic diffusion offer a very close analogy with those of the diffusion of gas from the molecular state at higher temperatures.

### Effect of Pressure.

The original observation of Cailletet that diffusion of nascent hydrogen would proceed against a considerable pressure of gas on the side of the metal not in contact with the solution, was confirmed by Bellati and Lussana,<sup>3</sup> and by Charpy and Bonnerot. Reverse pressures of the order of 20 atmospheres

<sup>1</sup> Charpy and Bonnerot, *C. Rend.*, 1912, 154, 592.

<sup>2</sup> Sutton and Taylor, *J. Inst. Met.*, 1934, 55, 149.

<sup>3</sup> Bellati and Lussana, *Atti del Reale Inst. Veneto Sci.*, 1890, 1, 1173.

were reached without any evidence that the rate of diffusion was reduced. Bardenhauer and Ploum<sup>1</sup> have observed diffusion through cast steel against pressures of 200 to 300 atmospheres, and it is probable that pressures of several thousand atmospheres could be attained. This is, of course, to be expected, since diffusion results from the difference in concentration of hydrogen *ions* on the two sides of the metal. At temperatures between 0° and 100° C. the rate of dissociation of molecular hydrogen in contact with the iron will be very small, whilst a high concentration of hydrogen ions is maintained by electrolysis on the other side. Winkelmann was unable to produce any effect by increasing the hydrostatic pressure on the solution, but this would naturally be negligible in comparison with the effect of the current density.

### Effect of Current Density.

The effect of current density on the rate of diffusion has been studied by several workers. It was shown by Bodenstein<sup>2</sup> that experimental results are well represented by an equation of the form

$$D = k \cdot \sqrt{I},$$

where  $I$  is the current density, which is conveniently measured in amperes per cm.<sup>2</sup> of surface. Since the concentration of hydrogen at the surface of the metal will be directly proportional to the current density, there is a close analogy with the gas pressure in the case of ordinary diffusion. Borelius and Lindblom<sup>3</sup> found the same departure from the square root law at low current densities that is observed at low gas pressures, and suggested the equation

$$D = k(\sqrt{I} - \sqrt{I_t}),$$

where  $I_t$  is a temperature-dependent threshold value of current density. There are no observations at sufficiently low current densities to establish the existence of a real threshold value,

<sup>1</sup> Bardenhauer and Ploum, *Mitt. Kais. W. Inst. Eisenf.*, 1934, 16, 129.

<sup>2</sup> Bodenstein, *Z. Electrochem.*, 1922, 28, 517.

<sup>3</sup> Borelius and Lindblom, *Annalen der Physik*, 1927, 82, 201.

and it seems more likely that the observed effect is due to the surface being incompletely covered by adsorbed gas at low currents, in the same way as in ordinary diffusion. Their

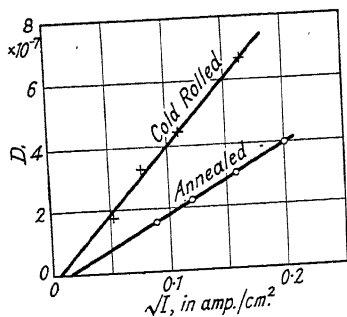


FIG. 87.—Effect of current density on electrolytic diffusion of hydrogen through 0.18 per cent. C steel.  
[Borelius and Lindblom.]

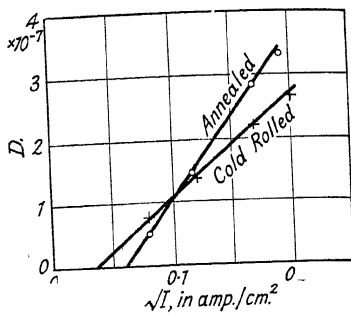


FIG. 88.—Effect of current density on electrolytic diffusion of hydrogen through 0.3 per cent. C steel.  
[Borelius and Lindblom.]

experimental observations are plotted in Figs. 87 and 88 for steel of two different carbon contents, in the annealed and “as rolled” condition.

### Effect of Voltage.

Winkelmann observed that the rate of diffusion was roughly proportional to the applied potential. The relation between the applied voltage,  $e$ , and the hydrogen-ion concentration is given by

$$e = 0.057 \log \frac{kC_H}{C_H},$$

so that, if diffusion is proportional to the hydrogen-ion concentration, we may write

$$\log D = \frac{e}{m} + a,$$

where  $a$  is a constant. Bodenstein found that this equation represented experimental results for different samples of iron, with values of  $m$  between 0.1 and 0.9, instead of 0.057. No other experimental evidence on this point is available.

### Effect of Temperature.

The rate of diffusion of hydrogen through iron at 20°, 60° and 97° C. was determined at various current densities by Borelius and Lindblom, and their results are plotted in the form of  $\log D - \frac{I}{T}$  curves in Fig. 89. It is clear that the effect of temperature is represented by the usual equation

$$D = k \cdot e^{-\frac{b}{T}}.$$

The value of  $b$  given by the slope of the lines in Fig. 89 is 4550, compared with 4700 found for gaseous diffusion at higher temperatures, and we may therefore conclude that the temperature coefficient is substantially the same in both cases. On this assumption, it is possible to find the gas pressure which is equivalent to any particular current density. In the case of iron and hydrogen we have

$$p = 17,000I.$$

when  $p$  is expressed in atmospheres and  $I$  in amps.

per cm.<sup>2</sup> It appears, therefore, that the diffusion of nascent hydrogen produced at the surface of a metal in an electrolyte is essentially the same process as the diffusion of molecular gas at higher temperatures. The dissociation of the gas is, however, brought about by chemical or electrochemical forces, and the hydrogen ions are readily adsorbed on the metal surface. Owing to the high concentration of ions maintained in this way, a relatively high rate of diffusion is observed at much lower temperatures than when the ions are produced by dissociation of molecules from the gas phase. On passing through the metal and emerging at the opposite surface, the hydrogen ions recombine to form molecular hydrogen. Attempts have been made to show that the hydrogen emerging

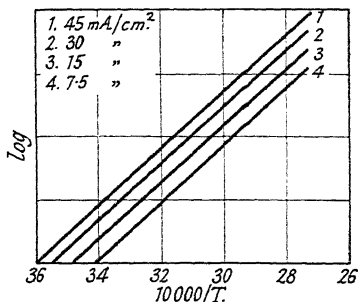


FIG. 89.—Effect of temperature on electrolytic diffusion of hydrogen through iron.

[Borelius and Lindblom.]

at this surface is in an active condition.<sup>1</sup> Whilst no reaction could be detected with bromine or sulphur, it reacts readily with oxygen to form water vapour. If a caustic soda solution is electrolysed in an iron tube, the outside of the tube rapidly tarnishes owing to the hydrogen combining with atmospheric oxygen.

Instead of electrolysing the solution, hydrogen may be evolved by the direct action of an acid on the metal, with similar results. Part of the hydrogen which is produced by the reaction diffuses into the metal. This may result in brittleness, or the production of small blisters on the surface. This is of practical importance in the steel industry, where it is customary to remove scale, etc., resulting from hot rolling, by

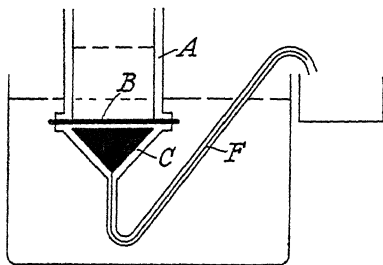


FIG. 90.

pickling the metal in an acid bath prior to tinning, enamelling or cold rolling. The factors affecting the diffusion of hydrogen under these conditions were first investigated by Edwards,<sup>2</sup> using the apparatus shown in Fig. 90. The metal sheet B is clamped between the glass cylinder A and the shallow funnel C, terminating in the capillary tube F. The funnel and capillary are completely filled with mercury, and the acid is poured into the cylinder A. Some of the hydrogen produced by the action of the acid diffuses through the metal sheet, and the displaced mercury is collected and weighed. The whole apparatus is immersed in a constant temperature bath. This method permitted the amount of hydrogen diffusing through the metal to be measured under various conditions. Edwards investigated the effect of changes in the concentration and kind of acid, temperature, thickness and state of the surface of the metal, on the amount of hydrogen diffusing. These factors also influenced the amount of hydrogen produced at the surface.

<sup>1</sup> Bodenstein, *loc. cit.* ; Morris, *J. Soc. Chem. Ind.*, 1935, 54, 7.

<sup>2</sup> Edwards, *J. Iron Steel Inst.*, 1924, 110, 9.

Of the total gas liberated at the surface of a metal sheet, 0.005 inch thick, the amount which diffused through varied from 0.5 per cent. at 55° C. to 3.0 per cent. at 100° C. The amount diffusing was roughly proportional to the temperature over this range, and inversely proportional to the thickness of the metal. The rate of diffusion was related to the concentration of the acid  $C$ , by the equation

$$D = k \cdot C^{0.417}.$$

Whilst the rate of diffusion, therefore, depends chiefly on the rate of production of hydrogen ions at the surface of the metal, it was also found to be affected by other conditions. For example, the rate of diffusion was about three times as fast with dilute sulphuric acid as with hydrochloric acid of equal concentration, but fell to about the same value when 5 per cent. of

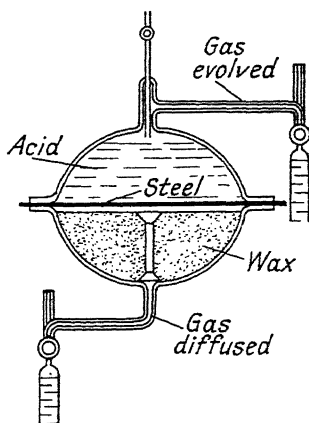


FIG. 91.

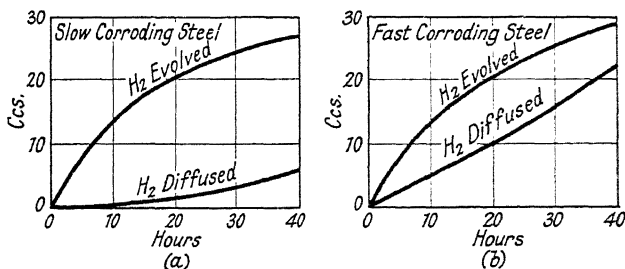


FIG. 92.—Hydrogen diffusion and evolution curves for steel in 1 per cent. citric acid solution at 25° C.

[Morris.

sodium chloride was added to the sulphuric acid. The rate of diffusion was also more rapid if the surface of the metal was covered with an oxide scale. These investigations have been confirmed and amplified by Morris<sup>1</sup> using citric acid solutions in the modified apparatus shown in Fig. 91, with

<sup>1</sup> *Loc. cit.*



which a direct comparison could be made between the hydrogen evolved as gas, and the hydrogen which diffused through the metal. Experiments with different steels showed that with fast corroding steel the rate of diffusion was increased more rapidly than the rate of evolution, as shown in Fig. 92.

Substances present in the electrolyte may influence the rate of diffusion. It is generally found that sulphur dioxide and arsenic trioxide increase the ratio of diffused to evolved gas, as seen in Fig. 93*a*, whilst inhibitors like gelatine or sugar have the reverse effect shown in Fig. 93*b*. Aten and Zieren<sup>1</sup> measured the rate of diffusion of hydrogen through iron electro-

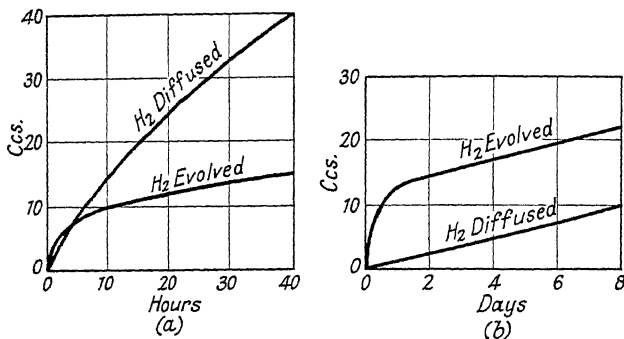


FIG. 93.—Hydrogen diffusion and evolution curves for steel in 1 per cent. citric acid containing (a) sulphur dioxide, (b) gelatin.

[Morris.

lysed in 0.1*N* NaOH solution, and found a large increase in the rate when either mercuric chloride or arsenic trioxide was added to the solution. A corresponding increase in the electrode potential occurred, as shown in Fig. 94, from which they concluded that the effect was due to a decrease in the rate of the conversion of H ions into molecules at the surface, thus effectively increasing the concentration of H ions. The effect was even more marked in sulphuric acid solutions. The effect of additions on the diffusion of hydrogen may also be disclosed by changes in the mechanical properties of steel subjected to cathodic polarisation. Alexejew and

<sup>1</sup> Aten and Zieren, *Rec. trav. chim.*, 1930, 49, 641.

Polukarow<sup>1</sup> used the arrangement shown in Fig. 95 in which a steel wire having a normal breaking strength of 62 kg. was loaded to 3 kg. When electrolysed with a current density of 0.1 amp./cm.<sup>2</sup> in pure caustic soda, the elastic properties and tensile strength remained unaltered for many hours, but in the presence of a trace of mercury the wires broke after about 30 minutes. Sulphur compounds present in an acid pickling

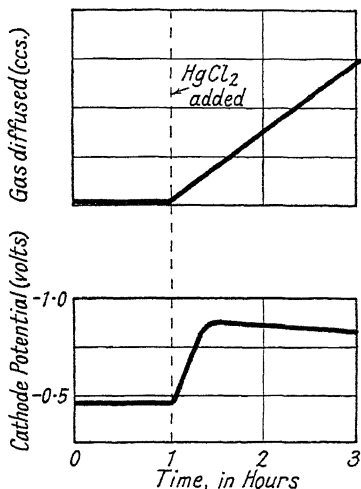


FIG. 94.—Effect of mercuric chloride in accelerating electrolytic diffusion of hydrogen through iron.

[Aten and Zieren.

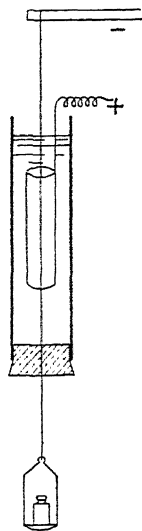


FIG. 95.

bath appear to have the same effect on steel sheet.<sup>2</sup> Excessive hydrogen adsorption produces the defect known as "grey sheet."

The facts just outlined regarding the diffusion of nascent hydrogen, whether produced by chemical or electrochemical attack, support the general theory of diffusion already discussed. Adsorption and ionisation of the gas on the metal surface are the controlling factors in ordinary diffusion, and account for the low rates at ordinary temperatures. The

<sup>1</sup> Alexejew and Polukarow, *Z. Electrochem.*, 1926, **32**, 248.

<sup>2</sup> Bablik, *Korr. u. Metallschutz*, 1935, **11**, 169.

relatively high rates of diffusion obtained with nascent hydrogen are due to the hydrogen being already ionised when it is produced at the surface, and therefore readily adsorbed.<sup>1</sup> The rate of diffusion is increased by any change which increases the concentration of hydrogen ions at the surface of the metal, but it may also be greatly affected by changes in the state of the surface. The catalytic poisons, which reduce the rate of ordinary diffusion, have their analogues in those substances which, by adsorption on the surface, inhibit corrosion. These substances, presumably by occupying the active centres, reduce the rate of diffusion even more than the rate of corrosion.

<sup>1</sup> See Farkas, *Trans. Faraday Soc.*, 1936, **32**, 1667.

## CHAPTER III.

## SOLUTION.

THE discovery that certain metals were permeable to hydrogen led Graham in 1866 to study the absorption of hydrogen by palladium. He found that palladium foil that had been heated in vacuo would absorb large quantities of hydrogen at ordinary temperatures, and over 900 times its own volume when heated in the gas. Graham introduced the word *occlusion* to describe the shutting up of gas in the metal in this way, but it is now more usual to speak of *absorption*, or simply *solution*. The palladium-hydrogen system is an exceptional one, for not only is the solubility much higher than for most gas-metal systems but it also varies in an abnormal manner with temperature and pressure. Very little attention was paid to other systems until nearly 50 years after Graham's pioneer work, and even now the work in this field is confined to one or two laboratories which have specialised in the subject. This is to be regretted, since a great deal of the published data must be accepted without the advantage of independent confirmation, which is particularly desirable when the experimental difficulties are great. Moreover, a great deal of the data on which we have to rely was obtained many years ago under experimental conditions which can no longer be considered reliable.

Our knowledge of the solubilities of gases in metals is derived partly from direct, and partly from indirect, observations. The direct observations consist in measuring the amount of gas absorbed by a known weight of metal under

definite conditions of temperature and pressure. The work of Sieverts and his school is far the most important in this field, and during the last 25 years a very large number of gas-metal systems have been carefully investigated at Jena. Similar methods have been used in a few instances by other workers. Mention may be made of the work of Röntgen and his colleagues on aluminium, and a number of contributions from the National Physical Laboratory. A large number of systems were investigated by Iwasé,<sup>1</sup> and his results have been frequently quoted. They have, however, failed to receive confirmation by other workers and the experimental methods, which are only briefly described, do not appear to have been very reliable.

Indirect information on solubility has been furnished in a number of ways. The work on diffusion described in the previous chapter throws some light on the problem of solubility. We have seen that gases can diffuse through metals, and that to do so they must become dissociated at the metal surface. Diffusion is caused by differences in concentration at different points in the metal, and therefore whenever diffusion can be detected we are justified in assuming that there must be some solubility, in the sense that the gas is present inside the metal in some form. The diffusion experiments help materially in understanding how the gas is distributed in the metal in different cases.

More important, perhaps, are measurements of the quantity and composition of gases which can be extracted from commercial metals. When heated *in vacuo* they give up considerable quantities of gas, which can be pumped away and analysed. The gas usually consists of mixtures of hydrogen, nitrogen, oxides of carbon and water vapour in various proportions. Sometimes hydrocarbons or sulphur dioxide are also found. These gases may not necessarily have been present in solution in the metal, and caution is necessary in drawing conclusions from these results. It is necessary to distinguish between the gas which has simply been adsorbed on the surface and that

<sup>1</sup> Iwasé, *Sci. Rep. Tohoku Imp. Univ.*, 1926, 15, 531.

which is derived from the body of the metal. In most, if not in all cases, the compound gases arise from combination, at the surface of the metal, of elements that have diffused separately. Oxygen and carbon, present in steel as oxides and carbides, may diffuse to the surface and combine to form CO and CO<sub>2</sub>. These gases are, therefore, obtained on heating the metal *in vacuo*.

### Definition of Solubility.

This raises the question of exactly what we propose to include in the study of the solubility of gases in metals. Broadly we mean the equilibrium conditions between the gas and the metal. This may involve the existence of one or more phases, and different types of equilibrium will be encountered. The gas absorbed by a metal may be dissociated and distributed as atoms throughout the metal lattice. This may be described as a simple solid solution, closely analogous to the solution of one metal in another. It was this analogy that led Graham to apply the name "hydrogenium" to hydrogen dissolved in palladium, indicating its metal-like properties. One point we shall have to consider is whether in such a solution the gas atoms replace the metal atoms in the lattice, as in metallic solid solutions, or whether they exist in the spaces between the metal atoms.

A gas may be absorbed by a metal with the formation of a definite compound, or it may be in true solution at one temperature, but form a compound if the temperature is changed. For example, oxygen dissolves readily in molten copper, but as soon as the metal freezes cuprous oxide is formed and can be observed under the microscope as a definite phase. In solid copper the bulk of the oxygen is therefore no longer in true solution in the metal, although if the metal is heated *in vacuo* at 1000° C. the whole of the oxygen can eventually be pumped away, since cuprous oxide has an appreciable dissociation pressure at this temperature.

Finally, we may have no solubility under any conditions. All these types of equilibria are met with in practice and must be taken into consideration.

### Experimental Methods.

The direct determination of solubility is usually made by exposing a weighed sample of metal to the gas at a known pressure and temperature until equilibrium is attained, and noting the volume of gas absorbed. In principle this is precisely the same as the method used in the measurement of adsorption, described in Chapter I. It is far more difficult, however, to obtain accurate measurements in the case of solution, for a number of reasons. In the first place, it is necessary to distinguish carefully between solution and adsorption. Solubilities are usually small, seldom exceeding a few cubic centimetres of gas per 100 grams of metal, whereas the amount adsorbed on the surface, in the case of metal powders, may be many times as great. It is desirable therefore to reduce the ratio of surface to volume of the specimen as far as possible. On the other hand, owing to the slow rate of the diffusion process it takes a very long time to reach equilibrium with samples of metal of appreciable thickness, and there is a great temptation to use metal in the form of thin foil or powder for this reason. Because of the small volumes of gas involved, large errors may be introduced by adsorption or evolution of gas by the walls of the apparatus. Solubility generally increases with temperature and is often only measurable above the melting-point of the metal, at temperatures that necessitate the use of silica or other refractory material for the apparatus. These materials are not entirely impervious to gases, and may be attacked by the metal at high temperatures. Equilibrium, except at high temperatures, is attained so slowly that many days may be required for each observation. Accurate results have only been obtained by very careful design of the apparatus and the use of modern high-vacuum technique.

### Apparatus and Method of Measurement.

The form of apparatus usually employed is essentially that of Sieverts,<sup>1</sup> and is in principle very simple. It is shown diagrammatically in Fig. 96.

<sup>1</sup> Sieverts, *Z. Metallk.*, 1929, 21, 37.

The metal is contained in a bulb of known capacity, which is connected to a vacuum pump, and also to a manometer and gas reservoir. The bulb A is evacuated, and a quantity of gas measured in the manometer B is admitted to it. At any temperature the pressure in the bulb can be calculated from the gas laws and any deviation from the expected value is due to absorption or evolution of gas by the metal.

Alternatively, the manometer may be calibrated so that the volume of gas in the apparatus can be read directly. The bulb A is surrounded by a furnace whose temperature is measured with a thermocouple, and a series of readings at various temperatures and pressures can be made without opening up the

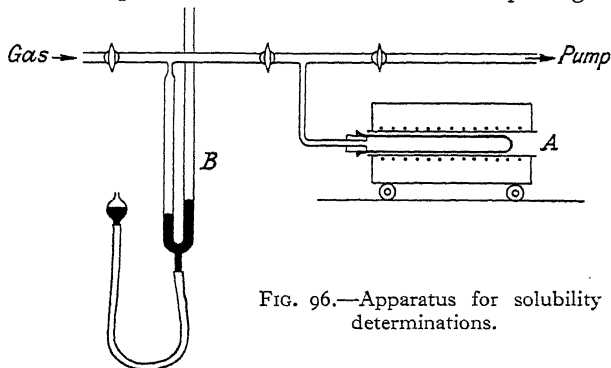


FIG. 96.—Apparatus for solubility determinations.

apparatus. Johnson<sup>1</sup> and his collaborators have used a modified form of this apparatus for determining the solubility of gases in gold and silver. A more accurate measurement of the final volume of the gas was obtained by correcting for the fact that the reaction bulb is at the furnace temperature whilst the gas in the remainder of the apparatus is at room temperature. This error is, of course, reduced by using small bore barometer tubing where possible. The actual pressure of gas measured in the manometer is given by the equation

$$p \left( \frac{V_1}{T_1} + \frac{V_2}{T_2} \right) = K,$$

where  $V_1$  is the volume of the reaction bulb at a temperature  $T_1$ ,

<sup>1</sup> Steacie and Johnson, *Proc. Roy. Soc.*, 1928, 117, 662 ; 1926, 112, 542 ; Toole and Johnson, *J. Phys. Chem.*, 1933, 37, 331.



and  $V_2$  is the volume of the rest of the apparatus at room temperature  $T_2$ .  $K$  can be calculated from the known volume of gas admitted, and hence the correct value of  $p$  obtained.

The furnace temperature was measured with a constant-volume nitrogen thermometer consisting of a silica bulb of approximately the same size as the reaction bulb. The two bulbs were placed side by side in the furnace, temperature variations in different parts being thus automatically compensated.

Braun<sup>1</sup> uses a slightly different method of measuring the

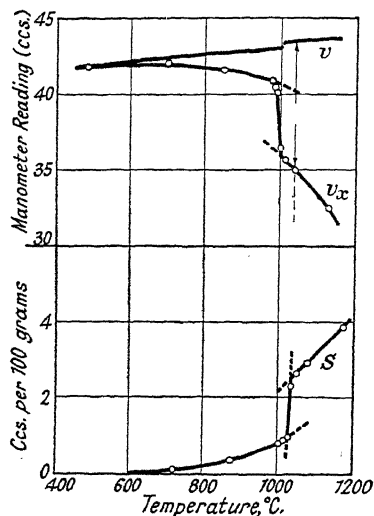


FIG. 97.

absorption. The reaction bulb may be used as a constant-pressure gas thermometer, and its linearity over the range of temperature used is checked by filling it with argon or nitrogen. Then when the bulb contains a sample of metal, any deviation from the straight line is due to absorption.

The accuracy of the thermocouple reading can be checked very readily at the melting-point, where the sudden change in the volume of the metal is re-

corded by the manometer. Typical observations on the absorption of hydrogen by a 6 per cent. aluminium copper alloy<sup>2</sup> are given in Fig. 97.

Curve  $v$  is the calibration of the empty bulb, and curve  $v_x$  the readings obtained with the metal sample. The solubility  $S$  is then given by

$$S = (v - v_x) \frac{t}{T},$$

where  $t$  is the observed temperature in degrees C.

<sup>1</sup> Braun, Dissert. Aachen., 1930.

<sup>2</sup> Röntgen and Möller, *Metallwirts.*, 1934, 13, 81.

This method of measurement was slightly modified by Bircumshaw,<sup>1</sup> who determined at each temperature

(a) the volume of hydrogen required to fill the reaction tube containing the boat only ;

(b) the volume required when the metal was placed in the boat.

The coefficient of expansion of the metal was also taken into account when allowing for the volume occupied by the metal at different temperatures.

*The Reaction Bulb.*—The most important feature in the absorption apparatus is the reaction bulb, which must be capable of withstanding the high temperatures involved, without becoming porous, reacting with the metal, or itself absorbing

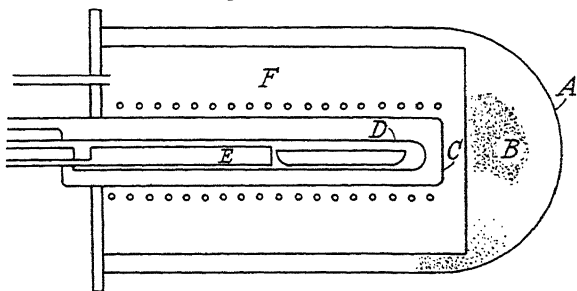


FIG. 98.—Absorption apparatus.

[Bircumshaw.]

appreciable quantities of gas. The upper limit to the temperature at which any material can be used may be determined either by softening and collapse, or by excessive permeability. Hard glass, such as pyrex, can be used up to 500° C., and clear silica up to 1000° C., but gases diffuse appreciably through both glass and quartz above a red heat. Silica is more satisfactory than glass, and the rate of diffusion is not appreciably affected by devitrification. Sieverts has used heat-resisting porcelain for temperatures up to 1200° C., and Bircumshaw found it satisfactory with hydrogen at temperatures up to 1000° C. To avoid loss of hydrogen by diffusion, however, he surrounded the reaction tube with an atmosphere of hydrogen, the arrangement being shown, somewhat simplified, in Fig. 98. A is an

<sup>1</sup> Bircumshaw, *Trans. Faraday Soc.*, 1935, 31, 1439.

iron container forming the body of the furnace, filled with thermal lagging B. The reaction tube D is surrounded by a silica tube C, and the space between them is filled with hydrogen. The dead space in D is largely occupied by the hollow silica plug E, also filled with hydrogen.

Röntgen and Möller recommend sintercorund<sup>1</sup> in preference to porcelain, and pythagoras tubing may also be used. In their experiments on the solubility of hydrogen in silver, Steacie and Johnson used a duplicate apparatus with an identical reaction bulb, which, however, was left empty instead of being filled with silver. The amount of hydrogen lost by diffusion through the "blank" bulb was applied as a correction to the volume measured in the reaction tube. The importance of this correction is shown by the fact that the volume of gas lost by diffusion varied from 20 per cent. to 50 per cent. of the volume actually absorbed by the silver, although the error is particularly large in this case, since the solubility of hydrogen in silver is small. With oxygen, a measurable, but much smaller, loss of gas was traced to oxidation of mercury vapour and tap grease.

*The Crucible.*—Whilst in some cases it is possible to heat the metal placed directly in the reaction tube, it is usually necessary to provide a crucible or boat of more refractory material, which will not react with the molten metal. Pure alumina is the most generally satisfactory material for this purpose, although each case requires special consideration. Magnesia should be used with the greatest caution. Although magnesia is a highly refractory material, it is far more easily reduced by metals than is generally recognised. Metals such as nickel, tungsten and molybdenum reduce magnesia quite readily at temperatures as low as 1400° C. Where the metal under investigation forms a refractory oxide, this is frequently the most suitable material to use as the crucible. Thus crucibles of alumina, zirconia and beryllia are inert towards the corresponding metals at all temperatures. Silica, on the other hand, is attacked by all the more reactive metals. The

<sup>1</sup> A refractory material manufactured by Messrs. Siemens and Halske.

form of the crucible should be such as to expose the largest surface of metal, so as to accelerate the attainment of equilibrium. The quantity of metal usually employed is from 20 to 200 grams, a large quantity helping to reduce errors due to adsorption on the walls of the apparatus.

*Preliminary Degassing.*—Before beginning an absorption measurement, the apparatus should be thoroughly degassed by prolonged evacuation, and all glass parts baked as far as possible during this process. Glass adsorbs large quantities of water vapour when exposed to the air and out-gassing may take several days in the first instance. Thereafter the apparatus should be opened to air as infrequently as possible, but when this is necessary the baking and exhaustion should be repeated. The reaction tube, crucible and metal sample should be thoroughly degassed at a temperature appreciably higher than that at which subsequent determinations are to be made. The problem of extracting gases already present in the metal is dealt with in greater detail in a later section (p. 198). The chief point to bear in mind is that degassing is essentially a diffusion process, and is completed more rapidly the higher the temperature. Whilst molten metal can be completely freed from gas in an hour or so, solid metals may require many days, and once this has been effected a series of measurements at different temperatures and pressures should be completed without opening the apparatus to the atmosphere. The actual time required for complete degassing depends very much on the apparatus and the amount of gas already in the sample. Braun, in his work on aluminium, exhausted for 12 hours at  $800^{\circ}\text{C}$ . Steacie and Johnson baked at  $550^{\circ}$ - $900^{\circ}\text{C}$ . for 8 hours, and again for 1 hour after standing overnight under vacuum.

*Rate of Absorption.*—After the degassing is complete, a measured quantity of gas is admitted to the reaction tube, and the temperature and pressure held constant until equilibrium is reached. It is obviously of the utmost importance to ensure that this is actually the case. The time required varies with the particular system, the form of the sample and the temperature. Equilibrium is reached much more rapidly above the melting-point than with solid metal.

In the case of molten metals, a few minutes may suffice. Röntgen and Braun<sup>1</sup> considered that equilibrium was reached instantaneously with hydrogen and molten aluminium. Bircumshaw found that with 35 grams of metal in a horizontal boat 1 minute was required at 1000° C., but that only 75 per cent. of the final absorption occurred in the first minute at 800° C., a further 15 minutes being required for the remainder. Some typical absorption-time curves are shown in Fig. 99. At temperatures as low as 200° C., many days may be required to reach saturation.

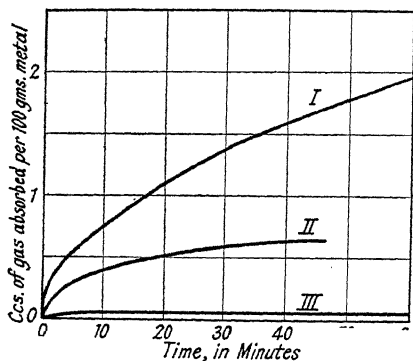


FIG. 99.—Rate of solution :

- I. Nitrogen in aluminium at 800° C., 760 mm.
- II. Oxygen in silver at 280° C., 336 mm.
- III. Hydrogen in silver at 700° C., 100 mm

The only satisfactory method of ensuring accuracy is to approach equilibrium from both higher and lower pressures, that is by absorption and by desorption. Only when values obtained by both the procedures are substantially the same can one be certain that equilibrium has been reached.

As a further check on the accuracy of the result, the remaining gas may be quickly pumped out, and the absorbed gas then recovered from the metal by pumping at a higher temperature. Steacie and Johnson recommend pumping out the whole of the gas, including that absorbed by the metal, and rejecting the determination unless the whole of the original quantity is recovered.

**Quenching Methods.**—Some qualitative information regarding the solubility of gases in molten metals has been obtained by very rapid cooling from above the melting-point. Lobley and Jepson<sup>2</sup> investigated the solubility of the common gases

<sup>1</sup> Röntgen and Braun, *Metallwirtsch.*, 1932, 11, 459.

<sup>2</sup> Lobley and Jepson, *J. Inst. Met.*, 1926, 35, 213.

in copper in this way. About 200 grams of metal were melted under reduced pressure in a resistance furnace, and a jet of hydrogen, nitrogen or carbon monoxide then directed onto the surface of the metal for 30 minutes. The crucible was then lowered rapidly into a water-cooled zone so that most of the evolved gas remained entrapped in the ingot. The volume of the blow-holes so formed was determined from density measurements. The soundness of the ingots obtained in carbon monoxide and nitrogen was taken to indicate that the solubility of these gases in the molten metal did not exceed that in the solid. Hydrogen, on the other hand, was evolved in large quantities on freezing.

Chipman and Murphy<sup>1</sup> determined the solubility of nitrogen in iron by holding the molten metal in contact with the gas, at temperatures between 1540° C. and 1760° C., until equilibrium was reached, and then cooling in nitrogen. The amount of nitrogen in the metal was then determined by analysis. This method is probably satisfactory when, as in this case, a definite compound is formed which does not readily decompose. It could not, however, be used for hydrogen, which would diffuse out of the metal during cooling.

*Electrolytic Methods.*—Certain metals absorb appreciable quantities of hydrogen when made the cathode in an electrolytic cell, and Graham's pioneer investigations of the absorption of hydrogen by palladium were carried out in this way. At the beginning of electrolysis practically no hydrogen is evolved, but it is absorbed by the metal, and only when the metal is saturated does evolution begin. The method is restricted to the very limited range of temperature in which aqueous solutions can be used, and the results are not directly comparable with ordinary measurements since the pressure, or concentration of gas at the metal surface, cannot be expressed in terms of gas pressure. It has, nevertheless, definite advantages for certain types of investigation. In measuring solubilities with molecular gas it is seldom possible to determine when equilibrium has been reached, at

<sup>1</sup> Chipman and Murphy, *Amer. Inst. Min. Met., Eng., Tech. Pub.* 591.

temperatures below  $200^{\circ}\text{C.}$ , owing to the excessive time required. The nascent hydrogen produced by electrolysis diffuses through the metal surface far more rapidly and this difficulty is overcome. For following the changes in such properties as electrical conductivity, or lattice parameter of the metal, with different concentrations of hydrogen, this method is ideal. It has been used with success in investigating the absorption of hydrogen by palladium and its alloys, a system which has been more intensively studied than any other, but with little success by the ordinary methods.

The procedure usually adopted was first described by Berry,<sup>1</sup> and the apparatus is shown in principle in Fig. 100.

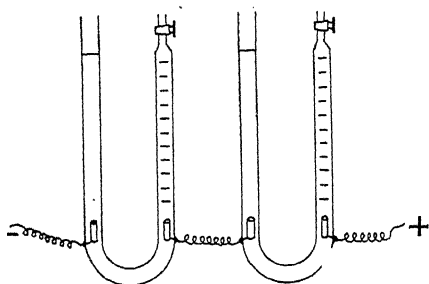


FIG. 100.

Two electrolytic cells, in the form of voltmeters, are arranged in series. The palladium under investigation is made the cathode in one cell, whilst the cathode in the other cell, and both the anodes, are made of platinum.

The hydrogen evolved in both cells is confined in graduated burettes. A 5 per cent. solution of sulphuric acid is a suitable electrolyte, and a current corresponding to about  $0.006\text{ amp./cm.}^2$  of cathode surface is passed in series through the two cells. The platinum absorbs no hydrogen, so that the volume absorbed by the palladium can be determined from the difference in the two burette readings. Krüger and Gehm,<sup>2</sup> who have carried out extensive investigations of palladium and its alloys by this method, used a wire of 1 mm. square section and 5 cm. in length as cathode. This was previously degassed for 6 hours *in vacuo* at  $750^{\circ}\text{C.}$  and quenched in water. At room temperature saturation was reached after 10 to 12 hours electrolysis. A particular feature of this method of charging metal with hydrogen is that the

<sup>1</sup> Berry, *J. Chem. Soc.*, 1911, 99, 463.

<sup>2</sup> Krüger and Gehm, *Annalen*, 1933, 16, 174 and 190.

process can be stopped when any desired concentration of gas has been reached.

The specimen can be again freed from absorbed gas by reversing the current, the oxygen which is now liberated at the surface of the palladium combining with the hydrogen to form water. One cannot be sure, however, that traces of hydrogen do not remain in the metal, and the alternative method of degassing by heating *in vacuo* is to be preferred.

### The Laws of Solubility.

Gas-metal systems, like any other heterogeneous equilibria, are subject to the phase rule, and might be treated in the same way as alloy systems. There is a certain resemblance in the types of system encountered, and some gas-metal systems can be regarded as simple solid solutions, whilst others involve the formation of compounds or new metallic phases. In the present state of knowledge, however, equilibrium diagrams have only a limited application.

The equilibrium conditions in gas-metal systems change with temperature, pressure, and the presence of other phases, such as alloying constituents, in the metal. In the case of simple solutions, the effect of some of these variables has been established, and definite laws enunciated. Where these simple laws are not followed it is generally due to the formation of compounds or new phases in the metal.

Of the common gases hydrogen is the most readily soluble in a large number of metals. Oxygen, although showing simple solubility in a few metals, more frequently gives rise to a definite oxide phase. Nitrogen is soluble in a limited number of metals, and although there is evidence of simple solubility in some cases, all metals which dissolve this gas are known to form definite nitrides under suitable conditions. The rare gases, so far as is known, are completely insoluble in all solid metals, but there may be some doubt regarding their solubility in some molten metals. We have already seen that compound gases can only diffuse into metals after dissociation, and we cannot therefore refer to simple solubility in these cases. As a rule these gases give rise to at least one compound. The



oxides of carbon may give rise to both oxides and carbides in the metal, hydrocarbons to dissolved hydrogen and a carbide phase, water vapour to hydrogen and an oxide phase. These systems are of the greatest practical importance, but so far have received very little attention and in hardly a single instance are the equilibrium conditions known.

The laws of solubility that have been established therefore relate almost entirely to metal-hydrogen systems, and are supported by a limited amount of data for oxygen- and nitrogen-metal systems.

### Effect of Temperature.

True solution is an endothermic process, and solubility therefore increases as the temperature is raised. As a rule

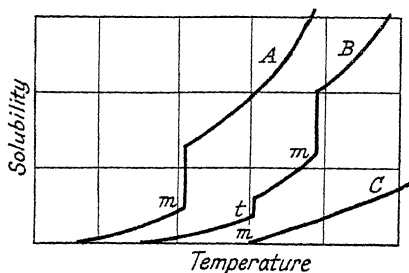


FIG. 101.—Types of absorption isobar.

gases are more soluble in liquid than in solid metals, and there is therefore a sudden increase in solubility at the melting-point. Solubility in the liquid metal also increases as the temperature is raised still further.

Since, in cases of true solution, the process is quite reversible, there is a sudden evolution of gas when the metal freezes. In Fig. 101 are shown different types of isobar which may be obtained with simple solutions. Curve A shows measurable solubility in the solid state, with a sudden increase at the melting-point  $m$ , and a rapid increase in solubility in the liquid metal as the temperature is raised still further. The isobar for hydrogen and copper is of this form. Curve B shows a similar system, but with a sudden increase in solubility at a transformation point  $t$ . Hydrogen is more soluble in  $\gamma$ -iron than in  $\alpha$ -iron, and the solubility curve therefore shows a discontinuity at the  $A_3$  point at  $900^\circ \text{C}$ . Curve C shows a system such as hydrogen and aluminium, in which the solubility in the solid metal is too small to be measurable, but

is appreciable in the molten metal. Further examples of these types will be found in the following pages.

Owing to the difficulty of making accurate measurements over an extended range of temperature, the exact form of the isobars is in many cases still uncertain. The experimental results are often sufficiently well represented by straight lines when the solubility  $S$  is plotted against the temperature  $T$ . Sieverts has usually presented his results in this way. Borelius<sup>1</sup> first pointed out that solubility should be related to temperature by an equation of the form

$$S = c \cdot e^{-\frac{E_s}{2RT}}, \quad (32)$$

where  $c$  is a constant and the exponent  $E_s$  represents the heat

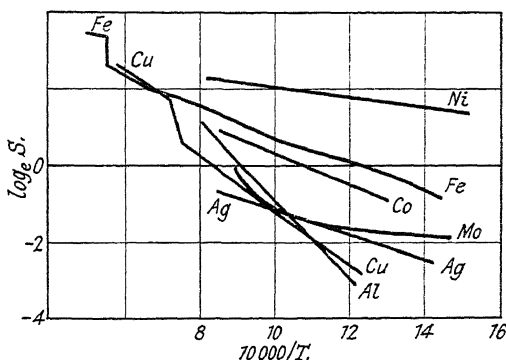


FIG. 102.—Effect of temperature on the solubility of hydrogen in metals.

of solution. If, therefore,  $\log S$  is plotted against  $1/T$  a straight line should be obtained. The data for a number of metal-hydrogen systems in which simple solution takes place are presented in this way in Fig. 102. It will be seen that in most cases the results are well represented by equation (32), when the probable accuracy of the experiments is taken into account. The heat of solution can be obtained from the slope of the  $\log S - 1/T$  plots. These are summarised in Table 12 (p. 152), and are seen to be of the same order as the heats of diffusion.

There is very little comparable data for simple solution of gases other than hydrogen, since in most cases oxygen and

<sup>1</sup> Borelius, *Annalen der Physik*, 1927, 83, 121.

nitrogen form definite compounds, but when they do not, the effect of temperature may be represented in a similar manner.

TABLE 12.

HEATS OF SOLUTION OF HYDROGEN IN METALS.

Metals.	$E_s$ . Cals./gm. mol. of $H_2$ .
Aluminium . . .	45,500
Silver . . . . .	11,600
Copper . . . . .	28,600
Nickel . . . . .	5,400
Cobalt . . . . .	17,000
Iron . . . . .	15,600
Molybdenum . . .	3,500
Platinum . . . .	35,400

There are a number of metal-hydrogen systems in which the solubility does not increase in a regular manner with the temperature. This can in most cases be attributed to the formation of definite hydrides. The evidence for the existence of such compounds is of various kinds. Whilst in simple solution the maximum quantity of gas taken up at atmospheric pressure corresponds to about one atom of hydrogen to 1000 atoms of metal, in the case of hydride forming metals the ratio is very nearly stoichiometric, being more nearly one or two atoms of hydrogen to each metal atom. The absorption is also accompanied by a very marked dilatation. The densities <sup>1</sup> of some of these metals and their hydrides are given in Table 13.

TABLE 13

Metal.	$\Delta_m$ .	Hydride.	$\Delta_H$ .	$\frac{\Delta_H}{\Delta_m}$ .
Titanium . . .	4.523	TiH <sub>2</sub>	3.91	0.864
Zirconium . .	6.53	ZrH <sub>2</sub>	5.67	0.867
Tantalum . . .	16.62	TaH	15.10	0.906
Vanadium . . .	6.11	VH	5.30	0.867

<sup>1</sup> Sieverts and Gotta, *Z. anorg. Chem.*, 1930, 187, 155; 1931, 199, 384.

It will be seen that there is a fairly constant increase in volume of about 15 per cent. X-ray pictures show that as hydrogen is absorbed the crystal lattice of the metal gradually expands, and although the exact position of the hydrogen atoms is not known, they must presumably take up positions between the metal atoms. Further evidence of compound formation is provided by the heats of absorption.<sup>1</sup> In the formation of  $TiH_2$  and  $ZrH_2$  there is an evolution of 36,000 and 40,500 calories/gram mol. respectively. These heats are comparable with the heats of formation of the hydrides of the alkaline earth metals. Since

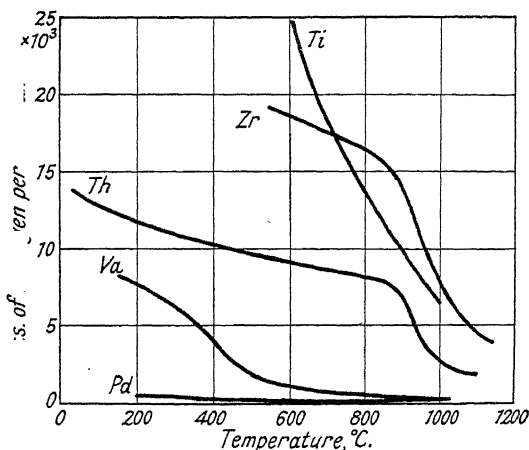


FIG. 103.—Absorption isobars for hydride forming metals.

in the cases under consideration there is an evolution of heat, solution has a negative temperature coefficient, and solubility decreases with rise in temperature. There is therefore a perfectly clear distinction between these systems and those in which only simple solution occurs. Some typical isobars of this kind are shown in Fig. 103. Absorption does not usually take place until a certain temperature is reached. For example, zirconium does not absorb hydrogen below about 700° C., nor does thorium below 400° C. If the metal is allowed to absorb hydrogen under these conditions until

<sup>1</sup> Sieverts and Gotta, *loc cit.*

equilibrium is reached, an amount corresponding very closely to the composition of the compound is taken up. At a pressure of 1 atmosphere Sieverts obtained absorptions corresponding to  $\text{ZrH}_{1.92}$ ,  $\text{TiH}_{1.76}$ ,  $\text{TaH}_{0.76}$ ,  $\text{ThH}_{3.07}$ , and  $\text{VH}_{0.72}$ . If the temperature is now raised, no further absorption is noted, but a gradual evolution of hydrogen. The temperature at which this begins to take place depends on the dissociation pressure of the hydride. The isobars may be represented by a  $\log S - 1/T$  plot, as in Fig. 104. Starting at the low temperature end (the right-hand side in Fig. 104), the curve remains horizontal until the hydride begins to decompose, and the solubility then decreases in accordance with equation (32). The temperature at which

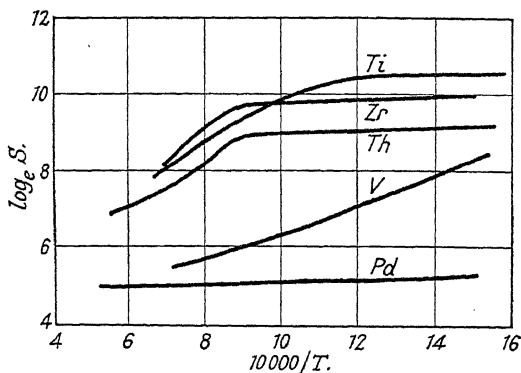


FIG. 104.

this occurs will naturally be lower, the lower the pressure at which the isobar is determined.

In many cases the isobars are complicated by the existence of different allotropic modifications of the metal at different temperatures, the hydrogen having different solubilities in the different phases. These will be considered later in discussing the individual systems.

Hydrogen does not in any case give rise to a compound which separates as a distinct phase visible under the microscope. On the other hand, with oxygen and nitrogen, when the solid solubility of the gas in the metal is exceeded, further absorption results in the formation of a second phase. The best-

known example of this is the copper-oxygen system. Oxygen is very soluble in liquid copper, but the solubility in solid copper is only about 0.015 per cent. at 1050° C. When copper which has been melted in air is allowed to freeze, the excess oxygen in solution is precipitated as a copper-cuprous oxide eutectic, and two phases are present in the solid metal. Cuprous oxide, which melts at 1235° C., is soluble in liquid copper, and forms with it a eutectic melting at 1065° C. containing about 3.5 per cent.  $\text{Cu}_2\text{O}$ . Systems of this kind are therefore complicated, and the effect of temperature is best represented by an equilibrium diagram of the conventional kind.

The silver-oxygen system is interesting and presents some unusual features. The solubility-temperature curve has a minimum at about 400° C. This means that the heat of solution is positive below 400° C. and negative at higher temperatures. Since the heat of formation of silver oxide is positive, whilst the heat of dissociation of oxygen is negative, this suggests that the oxygen is mainly present as silver oxide below this temperature, and as dissolved oxygen above 400° C. Silver oxide has a high dissociation pressure above 400° C., and the system therefore illustrates both true solution and compound formation according as the temperature range is above or below this value.<sup>1</sup>

### Effect of Pressure.

Sieverts has shown that in all cases of simple solution the absorption of gases is proportional to the square root of the gas pressure. Since we now know that the gas molecule is dissociated on solution, this result would be expected. This relation should hold good for any range of pressure in which

<sup>1</sup> The solubility of hydrogen in liquid ammonia, and of hydrogen, nitrogen, CO, and the noble gases in various organic liquids all show an increase in solubility with rising temperature (see Wiebe and Tremearne, *J. Amer. Chem. Soc.*, 1934, 56, 2357; Just, *Z. Phys. Chem.*, 1901, 37, 342). Curves for the solubility of hydrogen in water at high pressures show a minimum between 0° C. and 100° C., thus resembling the silver-oxygen system (Wiebe and Gaddy, *J. Amer. Chem. Soc.*, 1934, 56, 76).

the ratio of hydrogen to metal atoms is small. Under experimental conditions this ratio seldom exceeds 1 to 100 or 1 to 1000, and the square root law is found to apply to all cases of simple solution, not only of hydrogen, but of oxygen and nitrogen also. Some typical isotherms are given in Fig. 105. The concentration of gas in solution must be in equilibrium with the surface concentration of adsorbed atoms. We see at once, therefore, that when there is no adsorption there can be no solubility. This is confirmed by experiment, and metals can only dissolve those gases which they can hold by adsorption of the activated type. Thus the rare gases are not

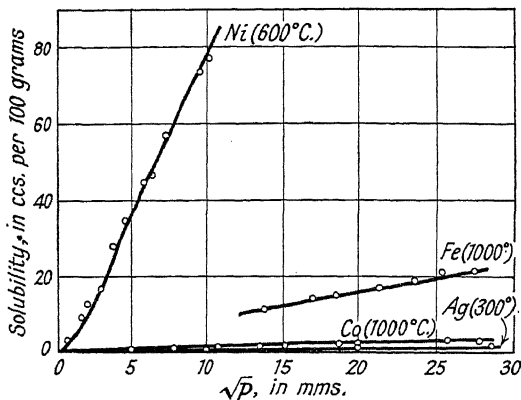


FIG. 105.—Absorption isotherms for hydrogen in nickel, iron, cobalt and silver plotted to show the  $\sqrt{p}$  law.

soluble in any metal, and nitrogen, for example, is insoluble in copper or silver. Since, as we have seen, adsorption is not rigidly proportional to the square root of the gas pressure at low pressures, we should expect solution to exhibit the same characteristic. Very few measurements of solubility have been made at low pressures, but the experimental results of Smittenburg<sup>1</sup> for nickel-hydrogen, and of Steacie and Johnson<sup>2</sup> for silver-oxygen, show the same deviation from the  $\sqrt{p}$  law at low pressures as are observed in the diffusion isotherms.

<sup>1</sup> Smittenburg, *Rec. trav. chim.*, 1934, **53**, 1065.

<sup>2</sup> Steacie and Johnson, *Proc. Roy. Soc.*, 1926, **112**, 542.

In cases of compound formation there will be an upper limit to the solubility, corresponding to the composition  $MH_n$ , when the metal is saturated, and further increase in pressure will not result in increased absorption. This is seen in the isotherms for hydrogen in zirconium, titanium, and the rare earth metals. Some of these isotherms are shown in Fig. 106. At low pressures absorption is proportional to the square root of the gas pressure, but falls off at higher pressures to an asymptotic value. The isotherms for palladium are somewhat unusual. At low pressures the square

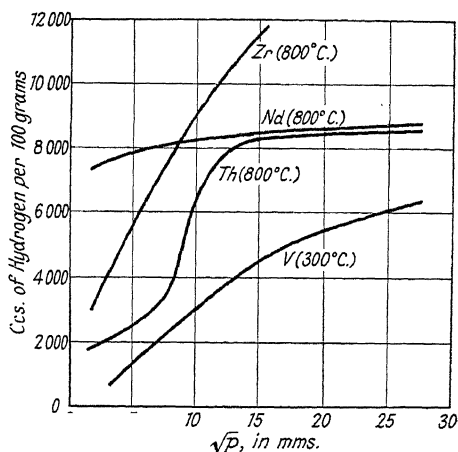


FIG. 106.—Hydrogen absorption isotherms for hydride forming metals.

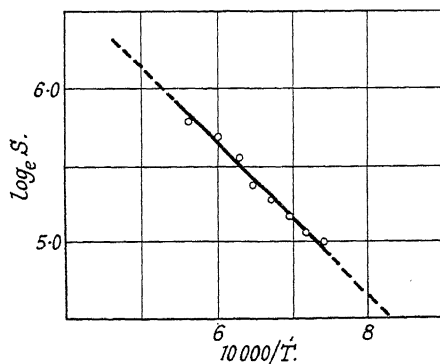


FIG. 107.  $\log S - 1/T$  plot for  $SO_2$  in copper.

[Stevarts.

root law is followed, until at a critical value, which depends on the temperature, gas is absorbed at constant pressure until saturation is reached. This is probably related to the dissociation pressure of a hypothetical hydride. This system, which is extremely complex, is discussed in more detail later.

Whilst in most cases the compound gases give rise to new phases, such as oxides or carbides, when they are absorbed by



metals, there is some evidence that they may exist in true

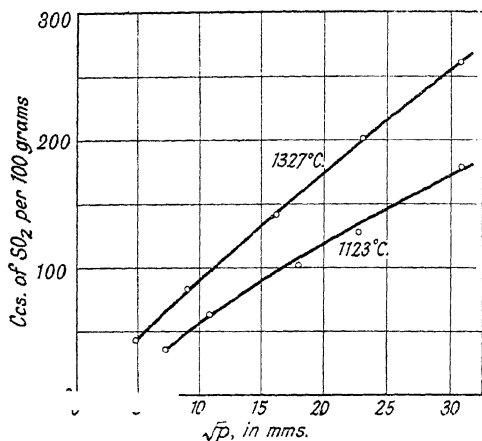


FIG. 108.—Solubility of SO<sub>2</sub> in copper plotted against the square root of the pressure.

with temperature, and the  $\log S \quad 1/T$  plot gives a straight line, as shown in Fig. 107. Sieverts concluded that the isotherms obeyed the square root law, and as shown in Fig. 108 they certainly appear to do so. This cannot, however, be explained in the usual way, for the equilibrium resulting from dissociation would give a cube root relationship. Sieverts' results have been plotted in this way in Fig. 109, and although the experi-

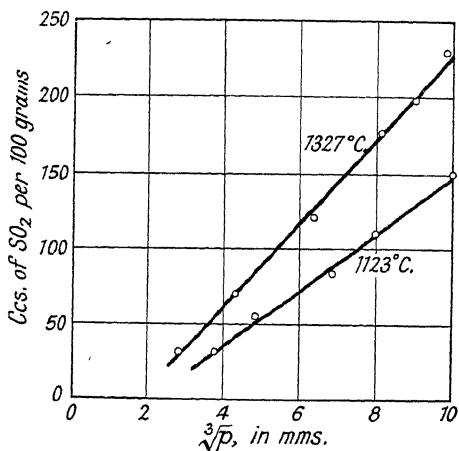


FIG. 109.—Solubility of SO<sub>2</sub> in copper plotted against the cube root of the pressure.

<sup>1</sup> Sieverts and Krumbharr, *Z. Phys. Chem.*, 1910, 74, 295.

mental points lie on very nearly straight lines, they do not pass through the origin. The square root law certainly seems to represent the results better, but no satisfactory interpretation of this can be offered.

The measurements of solubility for the various gas-metal systems that have been investigated are summarised below.

### Hydrogen.

The metals which absorb hydrogen may be divided into two groups :—

GROUP I.—Those metals in which the gas is in true solution,

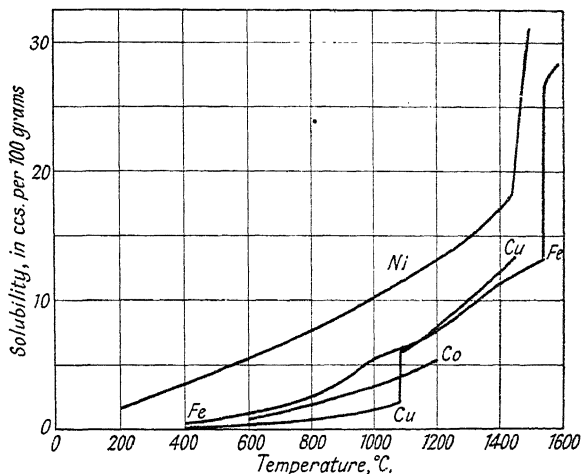


FIG. 110.—Solubility of hydrogen in nickel, iron, cobalt and copper.

and in which there is no evidence of the formation of compounds. Hydrogen is readily absorbed by iron, nickel, cobalt and copper in the solid state, and to a less extent by silver. There is a large increase in solubility when the metal melts. Molybdenum and platinum dissolve very small amounts of hydrogen in the solid state. Aluminium also belongs to this group, although the solubility in the solid metal is almost negligible. In these metals solution is a completely reversible process, the solubility is proportional to the square root of the gas pressure, and follows the exponential law given by

equation (32). Solution may be accompanied by a slight dilatation, but neither the mechanical nor the electrical properties are much affected. The most probable values for the solubilities at atmospheric pressure are plotted as a function of temperature in Figs. 110 and 111, and amplified by the notes given below.

GROUP 2.—The metals which form definite hydrides include the rare earth metals, Pd, Zr, Ti, V, Th and Ta. These metals may take up small amounts of hydrogen in true solution, the lattice being expanded a few per cent., without affecting the metallic properties. With large amounts of gas definite compounds are formed, but the process is still essentially reversible.

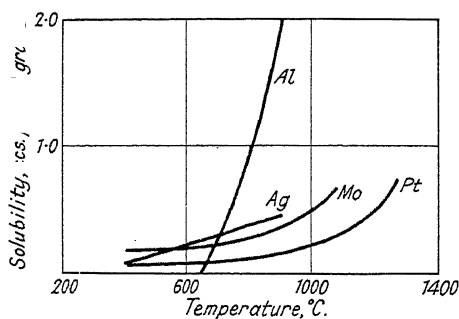


FIG. 111.—Solubility of hydrogen in aluminium, silver, platinum and molybdenum.

At temperatures between 300° and 800° C. gas is taken up very rapidly. X-ray examination often reveals a definite change in the lattice structure or the presence of a new phase. The electrical resistance increases, and the ductility is de-

creased. At high temperatures the hydrides decompose and gas is given off again. Metals which have been rendered brittle by absorption of hydrogen may recover their ductility on heating in vacuum, although this is not always the case. Sometimes the hydrides, which are electronic semi-conductors, have a characteristic appearance, but often there is no visible change when the gas is absorbed. The amount of hydrogen absorbed at atmospheric pressure is given for this group of metals as a function of temperature in Table 14. The absorption is not always proportional to  $\sqrt{p}$ , the shape of the isotherms depending on the phases present. The individual systems are discussed below.

GROUP 1 : *Aluminium*.—The solubility in molten aluminium

has been determined by Braun,<sup>1</sup> Röntgen and Braun,<sup>2</sup> Röntgen and Möller,<sup>3</sup> and Bircumshaw,<sup>4</sup> and their results are in very good agreement. With about 50 grams of metal, equilibrium is reached almost instantaneously at 1000° C., but at 800° C. about 15 minutes are required. The solubility in the solid metal is too small to be detected by the usual methods, and hydrogen is usually said to be insoluble. The fact that diffusion can be measured quite readily, however, proves that

TABLE 14.

ABSORPTION OF HYDROGEN BY METALS WHICH FORM HYDRIDES.

Temp., °C.	Hydrogen Solubility in c.c. per 100 gms. Metal.								
	Ce.	La.	Nb.	Pd.	Ta.	Th.	Ti.	Va.	Zr.
20	—	—	5,500	—	—	12,500	40,300	15,000	—
150	—	—	—	—	—	—	—	8,200	—
300	18,400	19,200	4,400	330	3,400	10,700	40,000	6,000	27,000
400	17,600	18,200	3,700	230	2,400	9,700	38,400	3,800	24,000
500	16,800	17,200	2,300	190	1,300	9,100	35,400	1,840	21,000
600	16,000	16,300	990	180	630	8,800	32,000	1,000	18,400
700	15,200	15,300	510	170	450	8,450	22,000	640	17,600
800	14,500	14,300	330	162	320	8,100	14,000	450	16,500
900	13,800	13,400	220	157	260	7,700	9,000	320	13,800
1,000	13,000	12,300	160	155	230	2,600	6,500	240	7,800
1,100	11,300	11,100	130	154	210	1,900	4,000	200	4,600
1,200	5,300	4,100	—	153	—	1,750	—	—	3,200

there must be some solubility. Hydrogen accounts for about 80 per cent. of the gas which can be extracted from commercial aluminium by vacuum treatment, although it cannot all be present in solution.

*Copper.*—The determinations of Röntgen and Möller<sup>3</sup> and of Sieverts<sup>5</sup> agree well at high temperatures, but differ by

<sup>1</sup> Braun, Dissert., Aachen, 1930.

<sup>2</sup> Röntgen and Braun, *Metallwirts.*, 1932, 11, 459.

<sup>3</sup> Röntgen and Möller, *ibid.*, 1934, 13, 81.

<sup>4</sup> Bircumshaw, *Trans. Faraday Soc.*, 1935, 31, 1439.

<sup>5</sup> Sieverts, *Z. phys. Chem.*, 1911, 77, 591.

about 2 to 1 at 500° C. They both show a very large increase in solubility at the melting-point. A hydride of copper,  $\text{CuH}$ , is known, and can be prepared by chemical methods<sup>1</sup> or by the action of atomic hydrogen on an activated copper surface.<sup>2</sup> The heat of formation is — 5120 calories, and the compound is very unstable. There is no evidence that it is formed by the action of molecular hydrogen on the metal.

*Silver*.—The solubility of hydrogen in silver<sup>3</sup> is only about half that in copper, the value of  $E_s$  being nearly the same in both cases. There are no data for the solubility above the melting-point.

*Iron*.—Hydrogen is more soluble in  $\gamma$  than in  $\alpha$ -iron, and there is therefore a discontinuity in the isobar at 900° C.<sup>4</sup> The presence of hydrogen in the metal increases the amount of heat generated in passing through the  $\text{Ar}_1$ ,  $\text{Ar}_2$ , and  $\text{Ar}_3$  points,<sup>5</sup> and in this respect hydrogen has the same effect as metals in solution. No information is available regarding the effect of carbon content or alloying constituents on the solubility of hydrogen in steels.

*Nickel*.—Nickel dissolves more hydrogen than any of the metals in this group, and there is a very large increase in solubility at the melting-point.<sup>6</sup> Although the existence of a hydride,  $\text{NiH}$ , has been established spectroscopically,<sup>7</sup> there is no indication from the solubility data that it is formed in the range of temperature and pressure under consideration.

*Cobalt*.—The solubility of hydrogen in cobalt<sup>8</sup> is very much less than in nickel, but increases more rapidly with temperature. There are no data for the solubility in the liquid metal.

<sup>1</sup> Sieverts and Gotta, *Ann. Chemie*, 1927, 453, 289.

<sup>2</sup> McMahon and Robinson, *J. Chem. Soc.*, 1934, 854.

<sup>3</sup> Steacie and Johnson, *Proc. Roy. Soc.*, 1928, 117, 662.

<sup>4</sup> Sieverts, *Z. phys. Chem.*, 1911, 77, 591.

<sup>5</sup> Roberts-Austin, 5th Report, Alloys Res. Com., 1899.

<sup>6</sup> Smittenburg, *Rec. trav. chim.*, 1934, 53, 1065.

<sup>7</sup> Gaydon and Pearce, *Nature*, 1934, 134, 287.

<sup>8</sup> Sieverts and Hagen, *Z. phys. Chem.*, 1934, 169, 237.

GROUP 2: *Palladium*.—Graham<sup>1</sup> observed in 1867 that palladium would absorb nearly 1000 times its own volume of hydrogen at room temperature, corresponding to an atomic ratio represented by  $\text{Pd}_2\text{H}$ . Since that time, numerous investigators have studied this system,<sup>2</sup> and although the absolute values of solubility at different temperatures and pressures have shown some divergence, the essential features of the system are generally agreed. The absorption of hydrogen has been studied both by electrolytic charging and with molecular hydrogen. The maximum absorption which can be obtained by electrolytic charging approaches the ratio  $\text{Pd}_2\text{H}$ , but at high gas pressures the limit is nearer to  $\text{PdH}$ . The solubility decreases rapidly as the temperature is raised, and the isobar for a pressure of 1 atmosphere is shown in Fig. 112. The isotherms present some striking features, as seen in Fig. 113. The isotherm consists of three parts:—

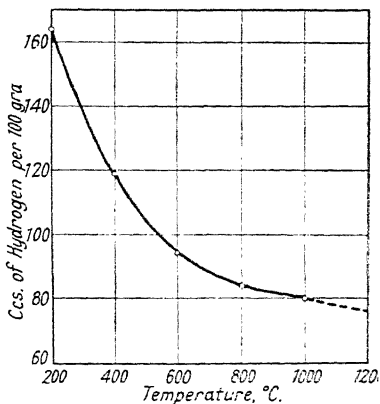


FIG. 112.—Absorption of hydrogen by palladium at 760 mm. pressure.

[Sieverts and Zapf.]

(a) at low pressures an absorption proportional to  $\sqrt{p}$ ;

(b) at a certain pressure, dependent on the temperature, a considerable absorption taking place at practically constant pressure;

(c) absorption again increasing with pressure at high pressures.

As the temperature is raised, the portion of the isotherm

<sup>1</sup> Graham, *J. Chem. Soc.*, 1867, 20, 270.

<sup>2</sup> Hagen and Sieverts, *Z. phys. Chem.*, 1933, 165, 1; Brüning and Sieverts, *Z. phys. Chem.*, 1933, 163, 409; Ubbelohde, *Trans. Faraday Soc.*, 1932, 28, 275; Ubbelohde and Egerton, *ibid.*, 284; Ipatieff and Tronow, *J. Phys. Chem.*, 1934, 38, 623; Hey, *J. Chem. Soc.*, 1935, 1254. For bibliography of earlier work see McKeehan, *Phys. Rev.*, 1923, 21, 334.

corresponding to (b) becomes shorter, occurs at a higher pressure, and eventually disappears. Adsorption is not per-

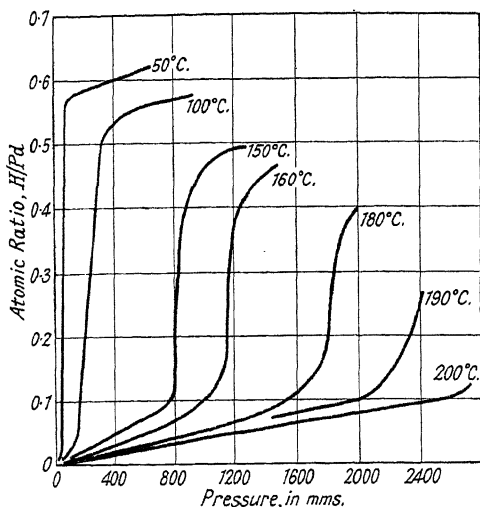


FIG. 113.—Isotherms for hydrogen-palladium.

fectly reversible in (b), but exhibits hysteresis as seen in Fig. 114. The absorption of hydrogen is accompanied by an expansion

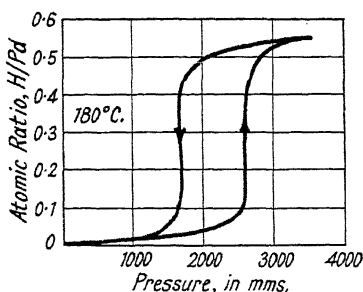


FIG. 114.—Absorption isotherm for hydrogen-palladium showing hysteresis.

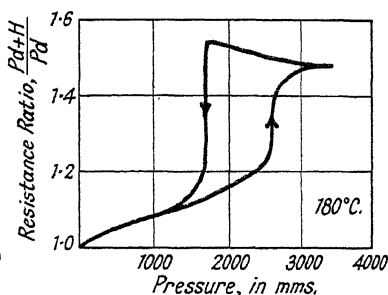


FIG. 115.—Resistance isotherm for hydrogen-palladium showing hysteresis.

of the metal of the order of 0.00004 cm. per cm. for each volume of gas absorbed. A marked increase in resistivity

also occurs, amounting to nearly 70 per cent. at saturation. If the ratio of the resistance of the hydrogen-charged metal to that of pure palladium is plotted against the pressure, a series of curves similar to the isotherms is obtained. These also exhibit hysteresis, as seen in Fig. 115. Considerable discussion has taken place as to the significance of the peculiar form of the isotherms and resistivity-curves. They are characteristic of a system consisting of two phases having a limited miscibility, and this explanation seems to be finally confirmed by the X-ray evidence.<sup>1</sup>

TABLE 15.  
LATTICE CONSTANTS FOR PALLADIUM-HYDROGEN.

Hydrogen Absorbed. H Atoms Pd Atoms	Lattice Constants, <i>a</i> .	Specific Resistance, ohm. cm.
0.0	3.884 —	$11.6 \times 10^{-4}$
0.11	3.886 —	12.7
0.23	3.886, 4.020	14.3
0.36	3.887, 4.020	15.3
0.56	3.886, 4.019	17.5
0.66	— 4.020	18.4
0.79	— 4.024	19.6
0.85	— 4.037	19.6
0.90	— 4.045	19.5

When hydrogen is absorbed by palladium the lattice is at first simply expanded. When the ratio of hydrogen to palladium atoms reaches about 0.2, new lines appear in the X-ray pattern, corresponding to a second expanded palladium lattice. Krüger and Gehm's measurements are given in Table 15, and shown diagrammatically in Fig. 116. It appears from these results that the hydrogen may enter the palladium lattice in two ways. One of these corresponds at saturation to  $\text{Pd}_4\text{H}$ , and the other to  $\text{PdH}$ . Over a certain range of concentration these two phases exist together, as shown by the shaded areas

<sup>1</sup> Linde and Borelius, *Ann. Physik*, 1927, 84, 747; Krüger and Gehm, *ibid.*, 1933, 16, 174.



in Fig. 117, where the resistivity and solubility data are presented together. The palladium-hydrogen system therefore

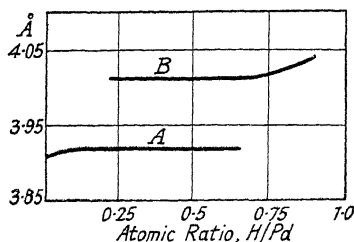


FIG. 116.—Lattice constants for hydrogen-charged palladium.

[Krüger and Gehm.

represents a link between the two groups of metals. The high absorption, approaching an atom to atom ratio, is characteristic of the hydride-forming metals. No new substance is formed,<sup>1</sup> however, but only two expanded palladium lattices representing solution characteristic of the first group. In the hydride-forming metals, of which tantalum is a typical example, the metal lattice may appear at each end of the system,

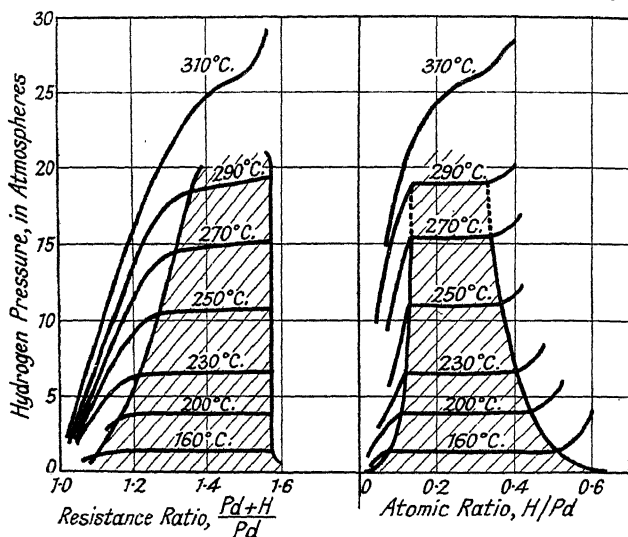


FIG. 117.—Absorption and resistance isotherms for hydrogen-palladium.

[Brinling and Sieverts.

separated by one or more phases having a different type of lattice.

<sup>1</sup> See, however, Gillespie and Galstraun (*J. Amer. Chem. Soc.*, 1936, 58, 2565) who conclude that four definite hydrides are formed.

The solubility of deuterium (heavy hydrogen) has been determined by Sieverts and Zapf<sup>1</sup> between 300° and 1100° C., and is compared with that of hydrogen in Table 16.

*Zirconium.*— $\alpha$ -Zirconium has a hexagonal structure,<sup>2</sup> but changes into the  $\beta$  form, having a body-centred cubic lattice, above 862° C. Hydrogen is rapidly absorbed above 800° C., the maximum absorption corresponding to  $\text{ZrH}_2$ , with an evolution of 40,500 calories per gram molecule of hydrogen absorbed.<sup>3</sup> Hydrogen is more soluble in the  $\beta$  than in the  $\alpha$  form, so that on cooling some gas is evolved on passing through

TABLE 16.

SOLUBILITY OF DEUTERIUM AND HYDROGEN IN PALLADIUM AT 760 MM.

Temperature, °C.	$S_H$ , c.c./100 gms.	$S_D$ , c.c./100 gms.	$\frac{S_D}{S_H}$
300	164	110	0.67
400	126	93.8	0.74
600	92.7	75.8	0.82
800	84.0	72.9	0.87
1000	78.5	71.5	0.91

the transition temperature.<sup>4</sup> Hägg<sup>5</sup> examined the system by X-ray methods and identified the phases given in Table 17.  $\alpha$ -Zirconium can dissolve up to 5 atomic per cent. of hydrogen, the lattice expanding about  $\frac{1}{2}$  per cent. Between 5 and 33 atomic per cent. there are 2 hexagonal phases present together, thus resembling the palladium-hydrogen system. Absorption is proportional to  $\sqrt{p}$  until saturation is reached, and is then independent of pressure.

*Titanium.*— $\alpha$ -Titanium, like  $\alpha$ -zirconium, has a hexagonal structure, and changes into the face-centred cubic  $\beta$ -phase

<sup>1</sup> Sieverts and Zapf, *Z. phys. Chem.*, 1935, **174**, 359.

<sup>2</sup> Vogel and Tonn, *Z. anorg. Chem.*, 1931, **202**, 292.

<sup>3</sup> Sieverts and Roell, *ibid.*, 1926, **153**, 289; Sieverts and Gotta, *ibid.*, 1930, **187**, 155.

<sup>4</sup> de Boer and Fast, *Rec. trav. chim.*, 1936, **55**, 350.

<sup>5</sup> Hägg, *Z. phys. Chem.*, 1931, **11**, 433.

above  $882^{\circ}\text{C}$ .<sup>1</sup> Hydrogen is absorbed rapidly by titanium powder above  $375^{\circ}\text{C}$ ., the maximum absorption corresponding

TABLE 17.  
PHASES IN THE ZIRCONIUM-HYDROGEN SYSTEM.

Phase.	Per Cent. Hydrogen Atoms.	Lattice Type.	Lattice Constants.		
			<i>a</i> .	<i>c</i> .	<i>c/a</i> .
$\alpha\text{-Zr}$ .	—	Hexa.	3.229	5.141	1.592
$\alpha\text{-solution}$ .	0.5	„	3.247	5.173	1.593
$\alpha + \gamma$ .	5.33	„	—	—	—
$\gamma$ .	33	„	3.337	5.454	1.635
$\delta$ .	50	f.c. cubic	4.766	—	—
$\epsilon(\text{ZrH}_2)$ .	66.6	f.c. tetrag.	4.964	4.440	0.894
$\beta(\text{Zr}_3\text{H})$ .	20.0	f.c. cubic	4.664	—	—

to  $\text{TiH}_{1.75}$ , with an evolution of 36,000 cal. per gram molecule of hydrogen. Two isobars are shown in Fig. 118.  $\alpha$ -Titanium

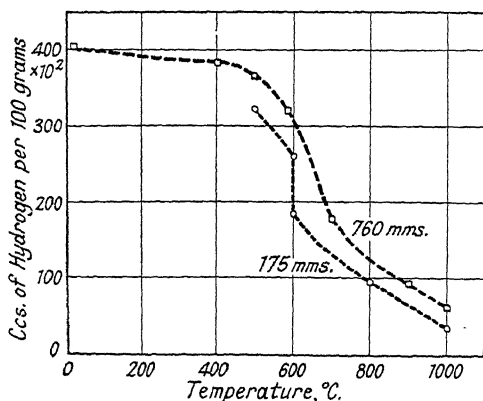


FIG. 118.—Isobars for hydrogen-titanium.

[Kirschfeld and Sieverts.]

can hold 33 atomic per cent. of hydrogen in solid solution. With more than 50 atomic per cent. a face-centred  $\beta$ -phase

<sup>1</sup> de Boer, Burgers and Fast, *Proc. K. Akad. Amst.*, 1936, 39, 515.

also appears.<sup>1</sup> The isotherms show that at low concentrations the  $\sqrt{p}$  law is obeyed.<sup>2</sup> A vertical part in the 600° C. isotherm indicates the co-existence of two phases.

*Tantalum*.—Tantalum absorbs hydrogen at temperatures above 400° C., and saturation approaches the composition TaH. The resistivity increases in direct proportion to the amount of hydrogen absorbed,<sup>3</sup> and at saturation is increased by 30 per cent. Hägg<sup>4</sup> has identified the following phases:—

- |   |                     |
|---|---------------------|
| $\alpha$ up to 12 atomic per cent. H                    | body-centred cubic. |
| $\beta$ (Ta <sub>2</sub> H) 12 to 33 atomic per cent. H | hexagonal.          |
| $\gamma$ (TaH) 33 to 50 atomic per cent. H              | body-centred cubic. |

Tantalum was discovered by Hatchett in 1801, and first prepared in a coherent form by von Bolton in 1904. The metal was invariably brittle, but it was found that bombardment with cathode rays, or fusion *in vacuo*, produced a ductile material. It is common experience that a drawn tantalum wire becomes brittle when heated in hydrogen,<sup>5</sup> and the ductility is not readily recovered. Recently, however, Moers<sup>6</sup> has found that tantalum prepared by thermal decomposition of the pentachloride is not made brittle by heating in hydrogen below 1450° C. If the wire is mechanically worked after deposition it then behaves like drawn wire, and becomes brittle at 700°-800° C. It would therefore appear that the degree of strain in the lattice affects the ease with which hydrogen is absorbed by the metal.

*Vanadium*,<sup>7</sup> *Thorium*,<sup>8</sup> and *Niobium*.<sup>9</sup>—These metals have similar characteristics to those of the preceding metals. The  $\sqrt{p}$  law is obeyed up to the saturated values corresponding to the respective hydrides. Vanadium becomes saturated at 300° C. Thorium absorbs hydrogen rapidly at 800° C., and is saturated at 100 mm. pressure at this temperature.

<sup>1</sup> Hägg, *loc. cit.*

<sup>2</sup> Kirschfeld and Sieverts, *Z. phys. Chem.*, 1929, 145, 227.

<sup>3</sup> Sieverts and Brüning, *ibid.*, 1935, 174, 365.

<sup>4</sup> Hägg, *loc. cit.*

<sup>5</sup> Burgers, *Z. anorg. Chem.*, 1934, 216, 223.

<sup>6</sup> Moers, *Metallwirtsch.*, 1934, 13, 640.

<sup>7</sup> Kirschfeld and Sieverts, *Z. Electrochem.*, 1930, 36, 123.

<sup>8</sup> Sieverts and Roell, *Z. anorg. Chem.*, 1926, 153, 289.

<sup>9</sup> Sieverts and Hagen, *ibid.*, 1929, 185, 225.

*Rare Earth Metals.*—The absorption of hydrogen by cerium,<sup>1</sup> lanthanum,<sup>1</sup> neodymium,<sup>2</sup> and praseodymium<sup>2</sup> is typical of the other metals in this group. At atmospheric pressure the metals remain saturated until the temperature exceeds 1000° C., since the hydrides are comparatively stable.

*Other Metals.*—No measurable solubility for hydrogen has been detected with germanium and indium.<sup>3</sup> There are a number of other metals, such as tin, zinc, etc., for which no reliable data are yet available.

## Nitrogen.

Nitrogen is only soluble in those metals which are capable of forming nitrides. We have previously noted the same distinction both in activated adsorption and diffusion, and the close connection between the three kinds of gas-metal equilibria is again emphasised. Nitrogen has been shown to be insoluble, within the limits of the experimental method, in cobalt,<sup>4</sup> copper,<sup>5</sup> silver,<sup>6</sup> and gold.<sup>7</sup> Those metals which, like iron and molybdenum, absorb nitrogen, show the same kind of changes in lattice structure, mechanical and electrical properties as are shown when the hydride-forming metals absorb hydrogen. The nitrogen-metal systems have not been investigated so completely as those of hydrogen, but the close parallel between them is evident from the data given below.

*Iron.*—Molecular nitrogen is not readily absorbed by iron unless the surface has been activated. Such activation may actually occur in service as the result of abrasion,<sup>8</sup> and the hardening of the surface so caused has been known to lead to failure.

Nitrogen is more readily absorbed if the metal is heated in ammonia. At temperatures above 350° C. iron powder reacts

<sup>1</sup> Sieverts and Roell, *Z. anorg. Chem.*, 1925, **146**, 149.

<sup>2</sup> *Ibid.*, 1926, **150**, 261.

<sup>3</sup> Sieverts and Hagen, *loc. cit.*

<sup>4</sup> Sieverts and Hagen, *Z. phys. Chem.*, 1934, **169**, 237.

<sup>5</sup> Lobley and Jepson, *J. Inst. Met.*, 1926, **35**, 213.

<sup>6</sup> Steacie and Johnson, *Proc. Roy. Soc.*, 1926, **112**, 542.

<sup>7</sup> Toole and Johnson, *J. Phys. Chem.*, 1933, **37**, 331.

<sup>8</sup> Schottky and Hiltenkamp, *Stahl u. Eisen*, 1936, **56**, 444.

rapidly, and the compact metal more slowly, the ammonia being decomposed at the surface. The solubility of nitrogen in iron has been investigated extensively<sup>1</sup> on account of the practical importance of nitrogen in steel. The most reliable values for the solubility at different temperatures, at a nitrogen pressure of 1 atmosphere, are given in Table 18.

Nitrogen is much more soluble in  $\gamma$ - than in  $\alpha$ -iron, and there appears to be an appreciable fall in solubility just below the melting-point. The solubility is greater in the liquid

TABLE 18.  
SOLUBILITY OF NITROGEN IN IRON AT 760 MM.

	Temperature, °C.	S, c.c./100 gms.
$\alpha$ . . .	750	0.32
	890	1.6
$\gamma$ . . .	900	20.0
	1300	17.5
	1390	16.6
$\delta$ . . .	1420	7.9
	1450	8.7
	1500	9.5
liquid . .	1540	24.5

than in the solid metal, and is, at all temperatures, proportional to the square root of the nitrogen pressure. The iron-nitrogen equilibrium beyond the limit of solid solubility has been determined by microscopic,<sup>2</sup> magnetic,<sup>3</sup> and X-ray methods.<sup>4</sup> The diagram, part of which is given in Fig. 119, indicates the existence of several phases. The lattice constants

<sup>1</sup> Fry, *Stahl v. Eisen*, 1923, 43, 1271; Köster, *Arch. Eisenhütt.*, 1931, 4, 537; Krüll, *Dissert.*, Jena, 1930; Sieverts and Zapf, *Z. phys. Chem.*, 1935, 172, 314; Sieverts, *ibid.*, 1931, 155, 299.

<sup>2</sup> Hensel and Larsen, *Metals and Alloys*, 1932, 3, 250.

<sup>3</sup> Lehrer, *Z. Electrochem.*, 1930, 36, 392.

<sup>4</sup> Eisenhütt and Kaupp, *ibid.*, 1930, 36, 392; Séférian, *Thesis*, Paris, 1934; Hägg, *Z. phys. Chem.*, 1930, 8, 455.

of these phases are given in Table 19, and the similarity to some of the metal-hydrogen systems will be noted.

TABLE 19.  
LATTICE CONSTANTS FOR IRON-NITROGEN SYSTEM.

Phase.	Atomic Per Cent. N <sub>2</sub> .	Lattice Type.	Lattice Constants in Å.		
			a.	b.	c.
$\alpha$ (solid solution)	0-20	b.c. cubic	2.86 to 2.871		
$\gamma$ (solid solution)	0-20	f.c. cubic	3.63 to 3.638		
$\gamma'$ (Fe <sub>4</sub> N) . . .	20	f.c. cubic	—		
$\epsilon$ (Fe <sub>3</sub> N) . . .	26-33	closed packed hex.	2.695 to 2.767		4.362 to 4.417
$\xi$ (Fe <sub>2</sub> N) . . .	33-	base cent. rhombic	2.758	4.819	4.419

Nitrogen may be absorbed by steel during arc welding, up to 0.15-0.2 per cent. by weight in the weld metal. The ab-

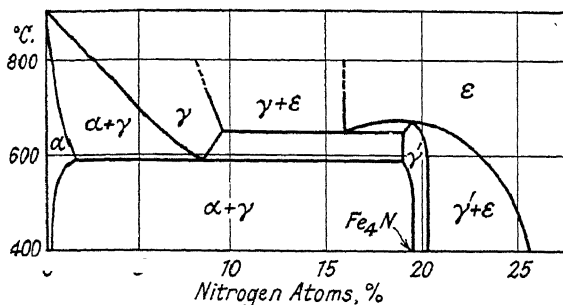


FIG. 119.—Iron-nitrogen equilibrium diagram.

[Séférián.]

sorption is less in oxy-acetylene welding, and seldom exceeds 0.02 per cent. N<sub>2</sub>. The nitrogen, if in excess of the solubility





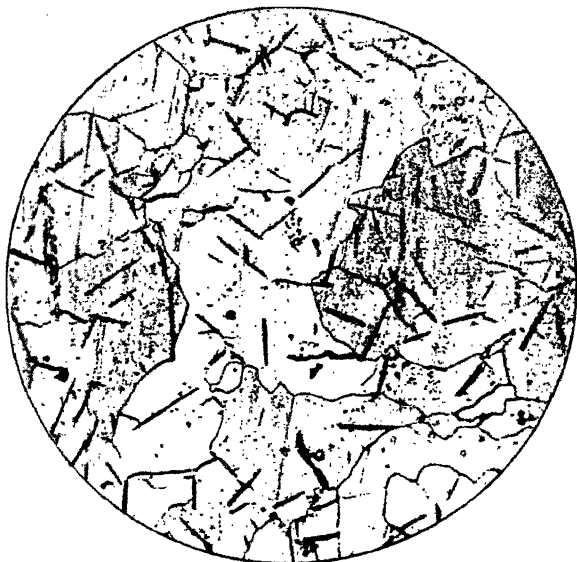


FIG. 120.—Needle crystals of  $\text{Fe}_4\text{N}$  in armco iron melted in an electric arc. Total nitrogen 0.10 per cent.  $\times 600$ .

[Séférian.]

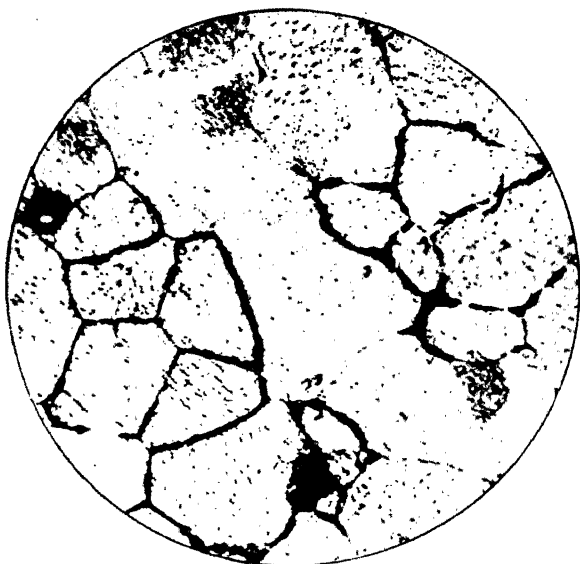


FIG. 121.— $\text{Fe}_4\text{N}$  precipitated in the grain boundaries by annealing at  $800^\circ\text{C}$ . Total nitrogen 0.18 per cent.  $\times 1500$ .

[Séférian.]

[To face page 173.]

limit (0.13 per cent.), separates as plate-like crystals of  $\text{Fe}_4\text{N}$ , as seen in Fig. 120.

Annealing at  $800^\circ\text{C}$ . results in precipitation of the nitride mainly in the grain boundaries, as in Fig. 121.

Nitrogen in steel produces austenitic and martensitic structures analogous to those produced by carbon. The Curie point is lowered by  $20^\circ\text{C}$ . The extreme hardness, characteristic of nitrides, is of considerable industrial importance, enabling a hard surface to be formed by the nitriding process.

*Molybdenum* —Sieverts<sup>1</sup> determined the solubility of nitrogen in molybdenum between  $936^\circ$  and  $1168^\circ\text{C}$ . The high solubility and negative temperature coefficient, seen in Table 20, clearly indicate compound formation.

TABLE 20.

SOLUBILITY OF NITROGEN IN MOLYBDENUM.

Temperature, $^\circ\text{C}$ .	S, c.c./100 gms.
950 . . . .	680
1000 . . . .	450
1050 . . . .	330
1100 . . . .	260
1150 . . . .	210

X-ray examination<sup>2</sup> of the molybdenum-nitrogen system reveals the following phases :—

$\alpha$  (Mo) body-centred cubic. No solid solution with nitrogen.

$\beta$  ( $\text{Mo}_3\text{N}$ ) face-centred tetragonal. Stable only above  $600^\circ\text{C}$ ., contains 28 atomic per cent. nitrogen.

$\gamma$  ( $\text{Mo}_2\text{N}$ ) face-centred cubic. Stable at all temperatures, contains 33 atomic per cent. nitrogen.

$\delta$  ( $\text{MoN}$ ) hexagonal, contains 50 atomic per cent. nitrogen.

Molybdenum wires heated for a few seconds in nitrogen at  $1300^\circ\text{C}$ . show marked changes in their mechanical properties.

<sup>1</sup> Sieverts and Bruning, *Arch. Eisenhütt.*, 1933, 7, 641.

<sup>2</sup> Hägg, *Z. phys. Chem.*, 1930, 7, 339.

The yield point is raised, and the elongation reduced from 40 per cent. to less than 5 per cent. The effect depends very much upon the condition of the wire, annealed wires nitriding much more readily than either cold worked or fully recrystallised metal.<sup>1</sup> The effect is probably due to surface hardening, since the resistivity is unchanged.

*Tungsten.*—Tungsten reacts very slowly to form the nitride  $W_2N$  at high temperatures, but no solid solutions are formed with nitrogen.<sup>2</sup>

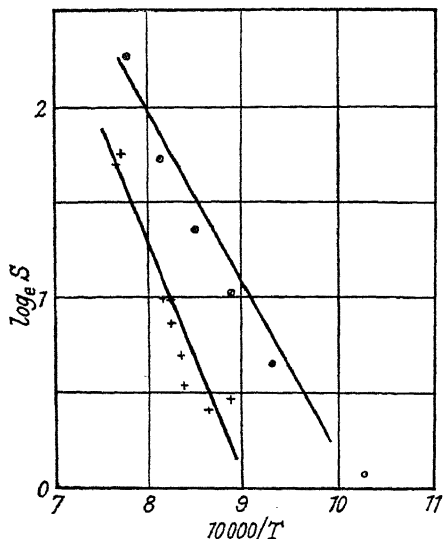


FIG. 122.— $-\log S - 1/T$  plot for nitrogen in aluminium.

○ Braun, + Röntgen and Möller.

*Aluminium.*—Nitrogen is soluble in molten aluminium,<sup>5</sup> and the solubility increases as the temperature is raised, as seen in Fig. 122. At the melting-point the molten metal can dissolve

*Manganese.*—The manganese - nitrogen system has been investigated by Hägg,<sup>3</sup> the X-ray evidence indicating the existence of 4 phases in the range of composition 0-14 per cent. N by weight, the phase diagram being very similar to that of the iron-nitrogen system. This has been confirmed by the determination of absorption isotherms.<sup>4</sup> There is no region of solid solubility.

<sup>1</sup> Túry and Krausz, *Nature*, 1936, 138, 331.

<sup>2</sup> Hägg, *Z. phys. Chem.*, 1930, 7, 339. Smithells and Rooksby, *J. Chem. Soc.*, 1927, 1882.

<sup>3</sup> Hägg, *Z. phys. Chem.*, 1929, 4, 346.

<sup>4</sup> Schenck and Kortengräber, *Z. anorg. Chem.*, 1933, 210, 273.

<sup>5</sup> Braun, Dissert., Aachen, 1930; Röntgen and Braun, *Metallwirtsch.*, 1932, 11, 459.

about 1 c.c./100 grams, but the solubility in the solid metal is probably very small. Aluminium nitride,  $\text{AlN}$ , is formed when the metal is heated in ammonia,<sup>1</sup> but it is unstable, and decomposes below the melting-point.

*Zirconium*.—Nitrogen is soluble up to 10 atomic per cent. in  $\alpha$ -zirconium, and the transition from  $\alpha$ - to  $\beta$ -zirconium then takes place over a range of several hundred degrees, instead of at a well-defined temperature.<sup>2</sup> The resistivity is increased by about 20 per cent. Dissolved oxygen has a very similar effect.

The change in resistivity as the result of nitriding in ammonia has been studied for a number of metals by Lafitte and Grandadam.<sup>3</sup>

## Oxygen.

Oxygen is soluble to some extent in most metals, but except in the case of the noble metals, an oxide phase also appears when the limit of solid solubility is exceeded. The solid solubility of oxygen in the common metals is usually considered as small in comparison with the total amount of oxygen which may be present in the metal. Many molten metals are capable of dissolving large quantities of oxygen (or of their own oxides, which amounts to the same thing), but on freezing the excess oxygen is precipitated as oxide. The solubility of oxygen in the solid metals is of the same order as that of hydrogen. It is, however, much more difficult to determine accurately. If the metal is allowed to absorb oxygen at a constant temperature and pressure, it is eventually converted into the oxide, and the solid solubility is not disclosed by this means. A sample of known oxygen content may be annealed at successively higher temperatures, and the lowest temperature at which it becomes homogeneous may be noted. This method is obviously unreliable where the solubility is small. An alternative method is to expose a sample of the metal to an oxidising atmosphere at a definite temperature until the interior is assumed to be saturated by diffusion, and then quench. The oxide scale is then removed,

<sup>1</sup> Saito and Okawa, *Chem. Abs.*, 1933, **27**, 1301.

<sup>2</sup> de Boer and Fast, *Rec. trav. chim.*, 1936, **55**, 459.

<sup>3</sup> Lafitte and Grandadam, *C. Rend.*, 1935, **200**, 1039.

and the concentration of oxygen in the core determined. This method also is obviously open to objection, since equilibrium may not have been reached, or quenching may not be effective. Neither method allows the accurate determination of solubility with varying temperature and pressure.

It appears probable that the usual laws relating to solubility are applicable. The  $\log S - 1/T$  relation has been established for silver and cobalt, and the  $\sqrt{p}$  law for silver. The most reliable data for the metal-oxygen systems are summarised below.

*Copper.*—The solid solubility of oxygen in copper has been determined between 600° C. and 1050° C. by Rhines and Mathewson,<sup>1</sup> with the results shown in Table 21.

TABLE 21.  
SOLUBILITY OF OXYGEN IN COPPER.

Temperature, °C.	Solubility.	
	C.c./100 gms.	Weight per cent. Oxygen.
600	5.0	0.0071
800	6.6	0.0094
950	7.0	0.0100
1050	10.9	0.0156

The equilibrium diagram for the copper-cuprous oxide system shown in Fig. 123 summarises the results of numerous investigations.<sup>2</sup>

*Iron.*—A constitutional diagram of the iron-oxygen system based on all previously published data was prepared by Benedicks and Lofquist<sup>3</sup> in 1927, and revised by Mathewson,

<sup>1</sup> Rhines and Mathewson, *Trans. A.I.M.E.*, 1934, 111, 337.

<sup>2</sup> Hanson, Marryat and Ford, *J. Inst. Met.*, 1923, 30, 197; Vogel and Pocher, *Z. Metallk.*, 1929, 21, 333; Allen and Street, *J. Inst. Met.*, 1933, 51, 233; Heyn, *Z. anorg. Chem.*, 1904, 39, 1; Slade and Farrow, *Proc. Roy. Soc.*, 1912, 87, 524.

<sup>3</sup> Benedicks and Lofquist, *Int. Conf. Test. Mat.*, Amsterdam, 1927, 1, 270.

Spire and Milligan <sup>1</sup> in 1931, as shown in Fig. 124. The solubility of oxygen in liquid iron <sup>2</sup> increases from 147 c.c./100 grams (0.21 per cent. O<sub>2</sub> by weight) at the melting-point to 387 c.c./100 grams (0.552 per cent. by weight) at 1734° C. Deter-

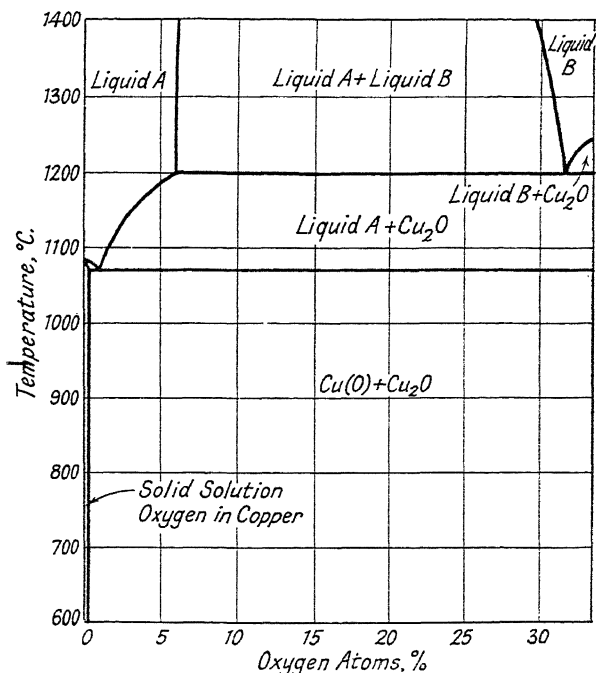


FIG. 123.—Copper-oxygen equilibrium diagram.

[Rhines and Mathewson.

minations of solid solubility show considerable differences.<sup>3</sup> Oxygen is probably more soluble in  $\gamma$ - than in  $\alpha$ - or  $\delta$ -iron, and estimates of the solubility in the region between 800° and 1000° C. vary from 24 to 28 c.c./100 grams (0.035-0.040 per

<sup>1</sup> Mathewson, Spire and Milligan, *Amer. Soc. Steel Treat.*, 1931, 19, 66.

<sup>2</sup> Herty, Gains, Larsen, Simkins, Geruso and Watkins, *Carnegie Inst. Tech.*, Bulletin 1927, 34, 1.

<sup>3</sup> See Tritton and Hanson, *J. Iron Steel Inst.*, 1924, 110, 90; Krings and Kempkens, *Z. anorg. Chem.*, 1930, 190, 313; Wimmer, *Stahl u. Eisen*, 1925, 45, 73; Oberhoffer, *ibid.*, 1927, 47, 1512.

cent. by weight). The solubility at the liquidus point on cooling is between 0.1 and 0.2 per cent. by weight. Oxygen lowers the  $A_2$  and  $A_3$  transformation points, but raises that of  $A_4$ .

*Cobalt.*—The solubility of oxygen in solid cobalt between 600° and 1500° C. has been determined by Seybolt and Mathewson.<sup>1</sup> Cobalt changes from the face-centered cubic

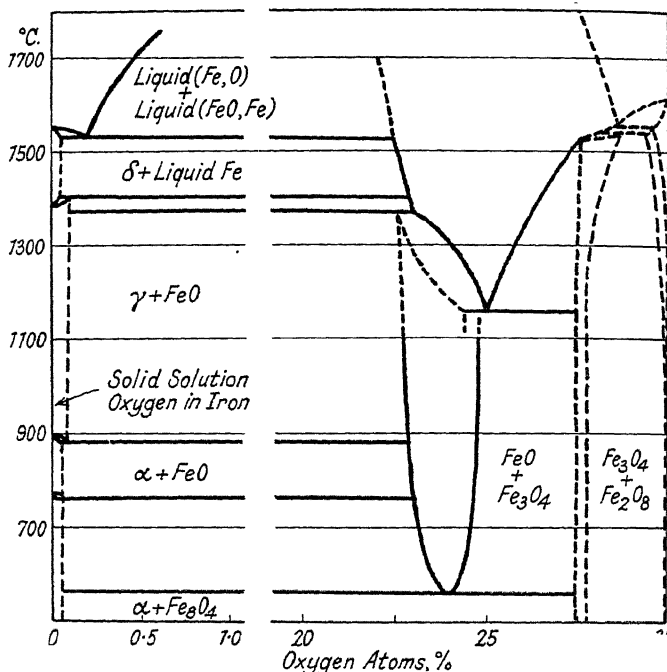


FIG. 124.—Iron-oxygen equilibrium diagram.

[Mathewson, Spire and Milligan.

( $\alpha$ ) form to the hexagonal ( $\beta$ ) phase at 850° C. The transition temperature is raised to 875° C. in the presence of dissolved oxygen. The solubility in both phases increases with the temperature, but there is a sudden decrease at the transition temperature, as shown in Fig. 125. The relation between  $\log S$  and  $1/T$  is linear in both phases.

<sup>1</sup> Seybolt and Mathewson, *Amer. Inst. Min. Met. Eng.*, Tech. Pub. 642, 1935.

*Nickel.*—Merica and Waltenburg<sup>1</sup> investigated the equilibrium in melts of nickel-nickel oxide. An eutectic melting at  $1438^{\circ}$  C. is formed with 1.1 per cent. NiO (0.24 per cent. oxygen), the melting-point of nickel being taken as  $1452^{\circ}$  C. No other oxide is present in the system up to 25 per cent. NiO. The solid solubility of oxygen in nickel has not been determined. Nickel containing oxygen up to the eutectic composition is malleable.

*Silver.*—The silver-oxygen system has attracted considerable attention because of the well-known phenomenon of "spitting," which takes place when silver is allowed to freeze after melting in contact

with the atmosphere. Molten silver absorbs about 20 times its own volume of oxygen,<sup>2</sup> that is 200 c.c./100 grams, at the melting-point, but the solubility falls very rapidly with the temperature. Steacie and Johnson,<sup>3</sup> who measured the solubility in solid silver, concluded that there was no abrupt change in solubility at the melting-point, but

merely that the curve was very steep in this region. The solubility  $50^{\circ}$  C. below the melting-point is only about 10 c.c./100 grams, and there is therefore a very large evolution of gas when the metal is solidifying. If, as is usually the case, a solid crust is formed on the surface of the ingot, the pressure of oxygen liberated in the interior ejects globules of the still molten metal. The solubility under various oxygen pressures is shown as a function of temperature in Fig. 126. The

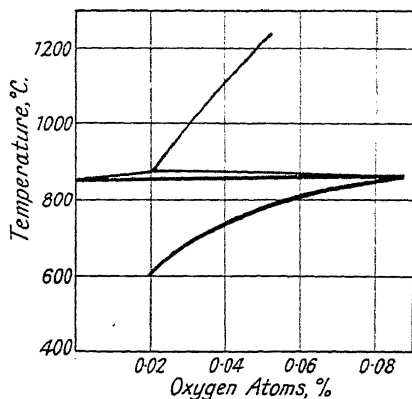


FIG. 125.—Cobalt-oxygen equilibrium.

[Seybolt and Matheisson.

<sup>1</sup> Merica and Waltenburg, *Bur. Standards Sci. Pap.*, 1925, 281.

<sup>2</sup> Sieverts and Hagenacker, *Z. phys. Chem.*, 1910, 68, 115.

<sup>3</sup> Steacie and Johnson, *Proc. Roy. Soc.*, 1926, 112, 542.



minimum point in the solubility curve at 400° C. is probably associated with the formation of a stable oxide  $\text{Ag}_2\text{O}$ , below

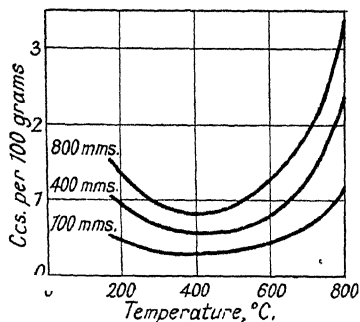


FIG. 126.—Solubility of oxygen in silver.

[Steacie and Johnson.

this temperature,<sup>1</sup> as indicated on page 155. Steacie and Johnson found that the solubility was proportional to  $\sqrt{p}$  at pressures above 10 mm.

*Other Metals.*—Practically nothing is known of the solubility of oxygen in the metals of less industrial importance. Oxygen appears to be soluble in zirconium<sup>2</sup> up to 10 atomic per cent., and produces the same effects as nitrogen.

Changes in the conductivity of palladium when made the anode in an electrolytic bath have been attributed to absorption of oxygen.<sup>3</sup>

### Effect of Structure and Composition.

Numerous examples will be found in the data just presented illustrating the effect of changes in crystal structure on the solubility of gases in metals. Where a metal may exist in more than one crystallographic form there is usually an abrupt change in solubility in passing from one phase to another. There is very little evidence regarding the effect of such structural differences as changes in grain size, cold working and annealing. If solution is a lattice phenomenon, these alterations in structure would not be expected to have any influence on solubility. From the fact that solubility determinations by different workers show good agreement, it appears that the form of the metal is unimportant. Thus Sieverts' values for the solubility of hydrogen in zirconium powder<sup>4</sup>

<sup>1</sup> Simons (*J. Phys. Chem.*, 1932, 36, 652) considers that the oxygen is present as  $\text{Ag}_2\text{O}$  in solution at all temperatures.

<sup>2</sup> de Boer and Fast, *Rec. trav. chim.*, 1936, 55, 459.

<sup>3</sup> D. P. Smith, *Zeit. Physik*, 1932, 78, 815.

<sup>4</sup> Sieverts and Roell, *Z. anorg. Chem.*, 1926, 153, 289.

agree well with those of de Boer and Fast<sup>1</sup> for zirconium wire prepared by deposition from the iodide. It has been suggested that gases may be more readily desorbed from metals that have been mechanically deformed, but this is not evidence of any change in solubility. On the other hand, Moers<sup>2</sup> found that tantalum wires prepared by thermal decomposition of the pentachloride do not absorb hydrogen below 1450° C., whereas drawn wire is rendered brittle when heated in hydrogen at much lower temperatures, and suggested that the undeformed metal has a much lower affinity for the gas than when it has been deformed.

Alloying constituents, or impurities present in the metal, which affect the lattice, may have a very marked effect on solubility. The effect of various additions to copper on the solubility of hydrogen has been investigated by Sieverts,<sup>3</sup> and his results are recorded in Fig. 127. Silver and gold have very little effect, nickel and platinum increase the amount absorbed, whilst it is reduced by aluminium and tin. It is probable that zinc also reduces the solubility in the molten metal, since even after bubbling hydrogen through molten brass there is no evidence of unsoundness in the ingots.<sup>4</sup> The

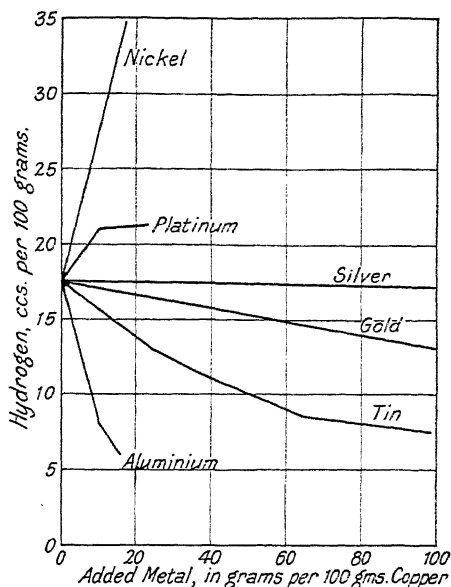


FIG. 127.—Effect of added elements on the solubility of hydrogen in copper.

[Sieverts.]

<sup>1</sup> de Boer and Fast, *Rec. trav. chim.*, 1936, 55, 350.

<sup>2</sup> Moers, *Metallwirt.*, 1934, 13, 640.

<sup>3</sup> Sieverts, *Z. Metallk.*, 1929, 21, 37.

<sup>4</sup> Bailey, *J. Inst. Met.*, 1928, 39, 191.

effect of aluminium has also been studied by Röntgen and Möller,<sup>1</sup> who found that the decrease in solubility was proportional to the amount of aluminium added. By extrapolation of the isotherms given in Fig. 128 it appears that the solubility in the molten metal would be reduced to zero by the addition of 30 atomic per cent. Al. This corresponds very

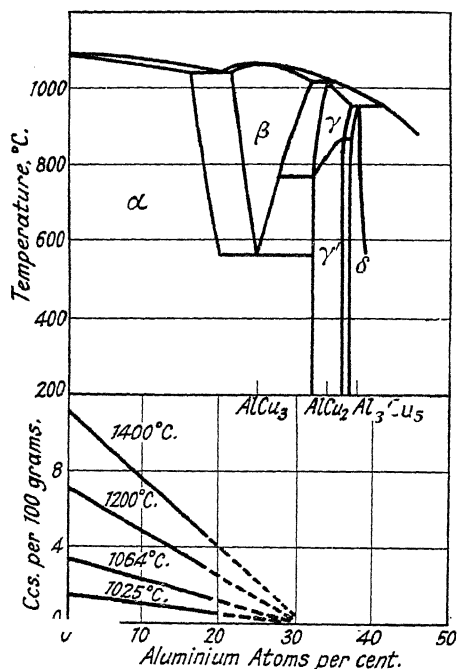


FIG. 128.—Solubility of hydrogen in aluminium-copper alloys.

[Röntgen and Möller.

closely with the  $\beta$ - $\gamma$  phase boundary, as seen from the equilibrium diagram given in the upper half of the figure. This correlation between solubility and phase changes in an alloy system is commonly to be observed, and corresponds to similar changes at transition points in pure metals. The addition of 3 per cent. of copper to pure aluminium also reduces the solubility of hydrogen in aluminium, from about 0.22 c.c./100 grams to 0.17 c.c./100 grams at the melting-point.

The effect of composition on the solubility of gases in steels has not received much attention. The effect of carbon content was investigated by Iwasé, but the results are not very conclusive. Sieverts' measurements of the solubility of hydrogen in iron have already been given in Fig. 102. Chipman and Murphy<sup>2</sup>

<sup>1</sup> Röntgen and Möller, *Metallwirt.*, 1934, 13, 81.

<sup>2</sup> Chipman and Murphy, *Amer. Inst. M. Met. Eng.*, Tech. Pub. No. 591.

found that the solubility of nitrogen in molten electrolytic iron was not influenced by the addition of 0.7 per cent. Si or 0.1 per cent. Al, but that these additions enormously increased the rate of absorption. This observation is consistent with the effect of other elements on the rate of diffusion of gases in steel, established by Bramley and discussed on page 122. Fukushima and Mitui<sup>1</sup> have determined the solubility of hydrogen in Cu-Ni, Fe-Co, Co-Cu, and Ni-Sb alloys.

The solubility of gases in a number of other alloy systems of less industrial importance has also been studied. In general, the observed changes in solubility as the composition is altered can be related to the constitutional diagram, and in some cases may actually provide a good guide to the phase changes which occur. The essential features of some of these systems may be summarised.

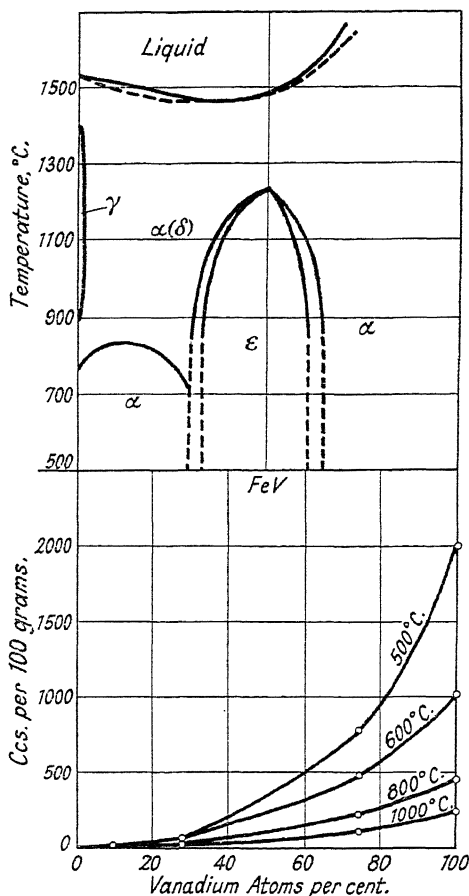


FIG. 129.—Solubility of hydrogen in iron-vanadium alloys.

[Kirschfeld and Sieverts.

<sup>1</sup> Fukushima and Mitui, *Sci. Rep. Tohoku Imp. Univ.*, 1936, 940.

*Iron-vanadium.*<sup>1</sup>—This system is of interest because, whilst vanadium forms a hydride and the absorption has a negative temperature coefficient, the solubility of hydrogen in iron increases with the temperature. The two metals form a continuous series of solid solutions, the equilibrium diagram being shown in the upper part of Fig. 129. In the lower part of this figure the isotherms for a pressure of one atmosphere are shown as a function of composition. Since, however, the solubility of hydrogen at low temperatures is about 10,000 times

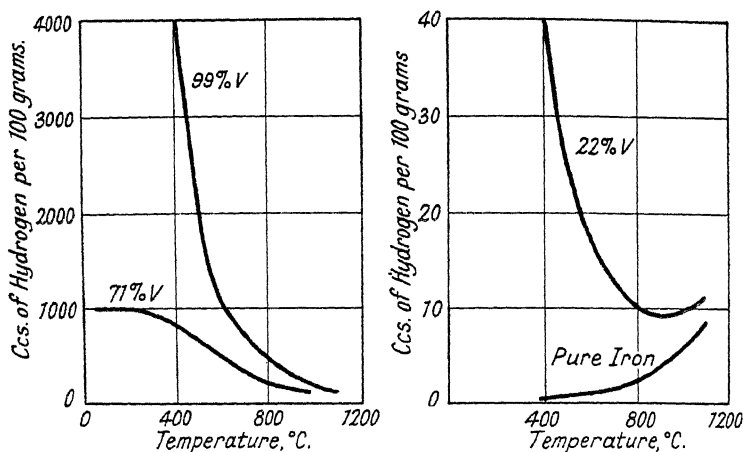


FIG. 130.—Absorption isobars for iron-vanadium alloys.

as great in vanadium as it is in iron, this figure only shows the general form of the isotherms. Fig. 130 shows that, at low temperatures, the alloys possess the high absorptive power of vanadium with quite small additions of that element, whilst at high temperatures the isobar is more nearly that of pure iron. Although not additive, the characteristic properties of each metal therefore appear in their alloys. Throughout the series the effect of pressure is satisfactorily represented by the square root law.

*Iron-molybdenum.*<sup>2</sup>—The equilibrium diagram in the upper

<sup>1</sup> Kirschfeld and Sieverts, *Z. Electrochem.*, 1930, 36, 123.

<sup>2</sup> Sieverts and Brüning, *Arch. Eisenhutt.*, 1933, 7, 641.

part of Fig. 131 shows the existence of a phase corresponding to the compound  $\text{Fe}_3\text{Mo}_2$ , at 40 atomic per cent. Mo. The solubility of hydrogen in iron is only slightly affected by the addition of molybdenum up to this amount, but thereafter decreases in almost linear relation to the molybdenum content. The temperature coefficient remains practically constant for all the alloys, as shown by the  $\log S - 1/T$  plot in Fig. 132.

The solubility of nitrogen is much greater in alloys containing  $\text{Fe}_3\text{Mo}_2$  (6-84 atomic per cent. Mo), than it is in the  $\alpha$ -phase. This is probably due to the formation of a complex nitride, which decomposes above  $1350^\circ\text{C}$ . Both gases obey the square root law throughout the series.

#### *Silver-gold.*<sup>1</sup>—

These metals form a continuous series of solid solutions. Oxygen is practically insoluble in solid gold, but readily soluble in silver, although the isobars have the peculiar form already discussed. The addition of gold to silver causes a reduction in the amount of oxygen

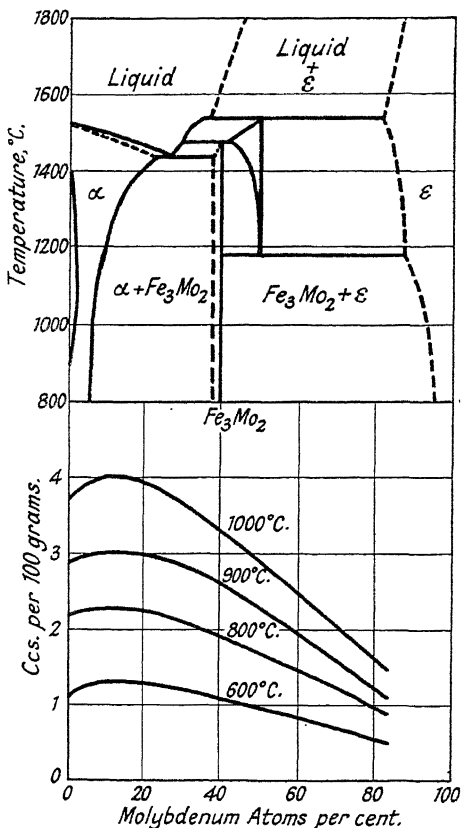


FIG. 131.—Solubility of hydrogen in iron-molybdenum alloys.

[Sieverts and Brüning.]

<sup>1</sup> Toole and Johnson, *J. Phys. Chem.*, 1933, 37, 331.

absorbed, and with 20 per cent. Au the minimum occurs in a much less pronounced form at about  $700^{\circ}\text{C.}$ , as seen in Fig. 133.

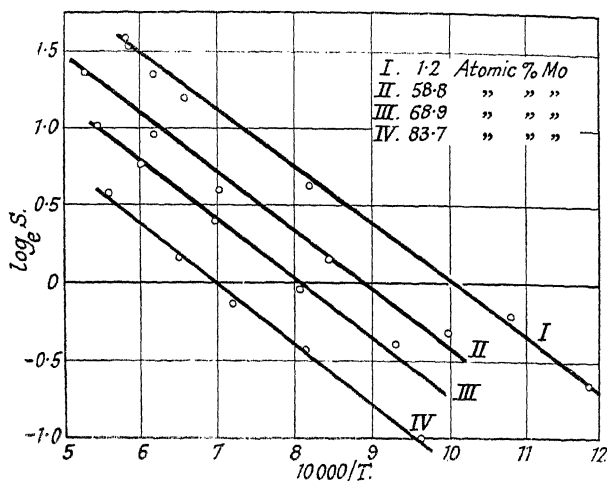


FIG. 132.—Log  $S - 1/T$  plots for hydrogen in iron-molybdenum alloys.

Above this temperature the  $\sqrt{p}$  law is obeyed, but below  $700^{\circ}\text{C.}$  the solubility is proportional to  $p^x$ , where  $x$  is less than 0.5. The

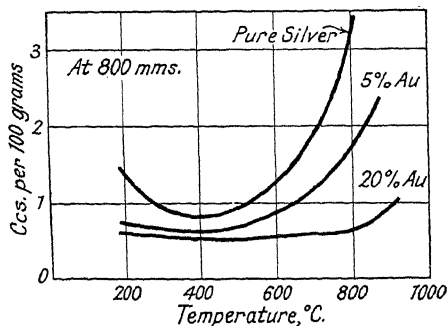


FIG. 133.—Solubility of oxygen in silver-gold alloys.

isotherms at various pressures are plotted below the equilibrium diagram in Fig. 134. Nitrogen, which is insoluble in both metals, is insoluble in the alloys.

#### Silver - copper. —

The absorption of oxygen by molten silver is not affected by the presence of

small amounts of copper, but this metal is often added to enable sound castings to be made.<sup>1</sup> The oxygen absorbed by the silver

<sup>1</sup> Streicher, *Z. Metallk.*, 1927, 19, 205.

combines with the copper to form cuprous oxide which is much more stable than silver oxide, so that the evolution of oxygen on freezing is avoided. Silver containing 1 per cent. of copper, after melting in air, solidifies without "spitting," whereas this is difficult to avoid with pure silver even under a covering of charcoal.

*Palladium Alloys.*—The solubility of hydrogen in a number of palladium alloys has been studied, a particular interest attaching to these systems owing to the abnormally high solubility of hydrogen in this metal.

Palladium and platinum probably form a continuous series of solid solutions. The solubility of hydrogen in platinum is very small, being only about  $1/4000$  that in palladium. The isotherms for one atmosphere,<sup>1</sup> for a series of alloys containing up to 50 per cent. platinum, are given in Fig. 135, and show a rapid fall in solubility with increase in platinum content. The solubility in this case is therefore a direct function of composition.

Palladium also forms a continuous series of solid solutions with silver and gold, both of which have practically no solvent power for hydrogen. The solubility-composition isotherms are, however, quite different from those for the Pd-Pt alloys. Instead of a gradual decrease, the solubility rises to a maximum

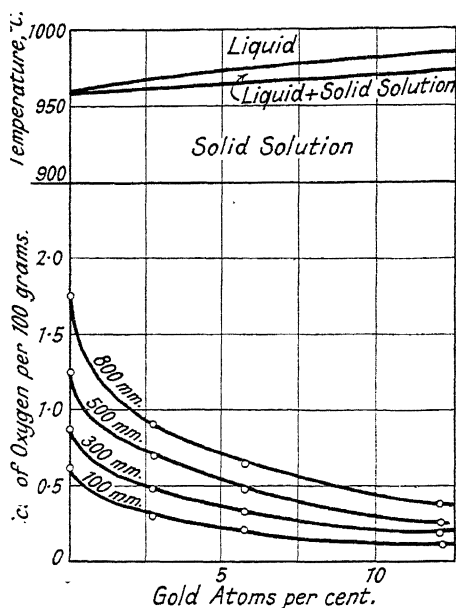


FIG. 134.—Effect of pressure on the solubility of oxygen in silver-gold alloys at 800° C.

<sup>1</sup> Sieverts, *Z. Metallk.*, 1929, 21, 37.



with 30-40 atomic per cent. of either silver or gold, and then falls, as seen in Figs. 136 and 137. As with pure palladium X-ray examination reveals the presence of two hydrogen-

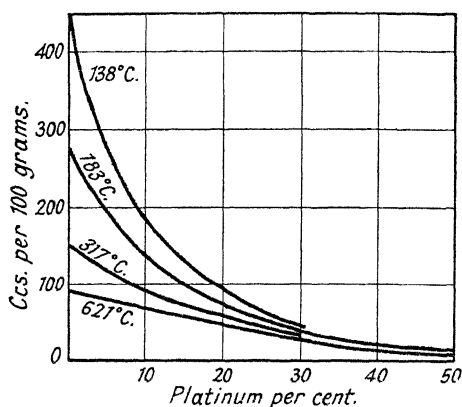


FIG. 135.—Solubility of hydrogen in platinum-palladium alloys.  
[Sieverts.]

containing phases having different lattice constants.<sup>1</sup> As the silver content of the alloy is increased, the parameters of the

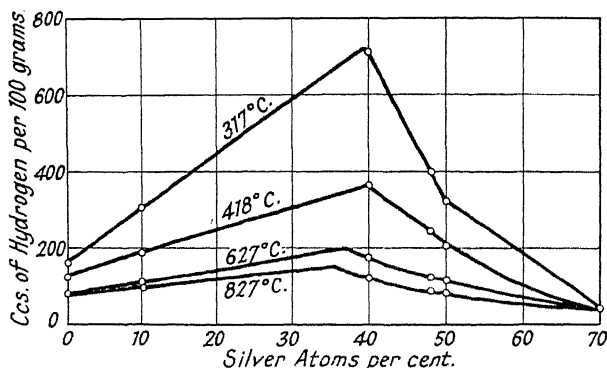


FIG. 136.—Solubility of hydrogen in silver-palladium alloys.

two phases become more nearly the same, and above 40 per cent. silver only one phase exists. These changes are shown

<sup>1</sup> Krüger and Gehm, *Annalen der Physik*, 1933, 16, 190.

in Fig. 138. Precisely similar curves were obtained by Mundt<sup>1</sup> for the corresponding gold alloys. Electrical resistance measurements show for each alloy an initial increase in resistivity with

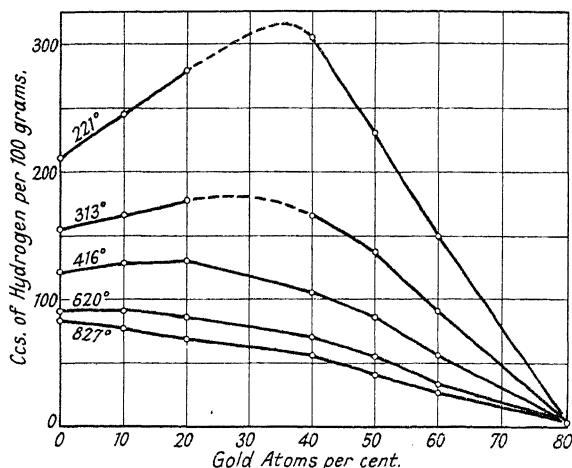


FIG. 137.—Solubility of hydrogen in gold-palladium alloys.

increase in hydrogen content, but at pressures of several atmospheres the resistivity falls again, and in a certain range of

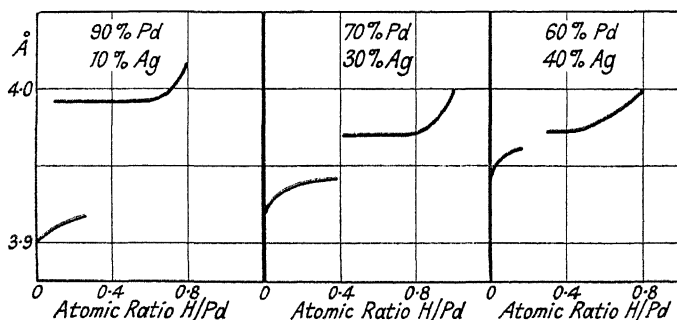


FIG. 138.—Lattice constants of hydrogen-charged silver-palladium alloys.  
[Krieger and Gehm.]

temperature and pressure it is possible to obtain a lower resistance for the gassed than for the gas-free alloy. The curves in

<sup>1</sup> Mundt, *Annalen der Physik*, 1934, 19, 721.

Fig. 139 show the change in resistivity with increase in the amount of hydrogen absorbed.<sup>1</sup>

Boron is soluble in palladium<sup>2</sup> up to about 6.9 atomic per cent., but with higher boron content the alloys have a duplex structure. At temperatures above 160° C. the solubility of hydrogen increases with the boron content up to 6.9 per cent.,

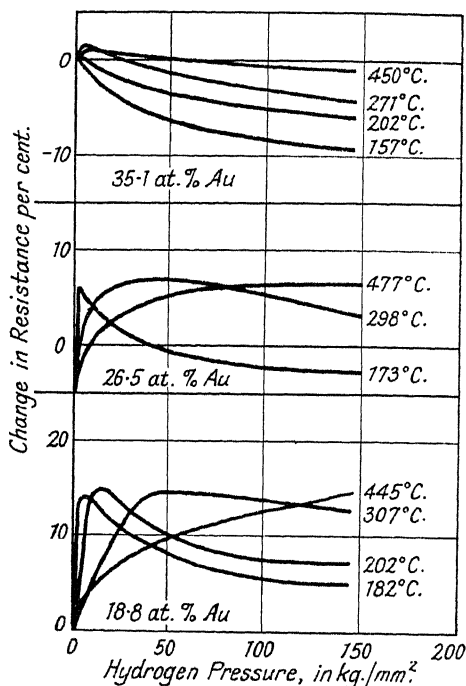


FIG. 139.—Change in resistance of silver-palladium alloys in hydrogen.  
[Sieverts and Hagen.

and then falls, the isotherms shown in Fig. 140 resembling those for the Pd-Ag and Pd-Au systems. Below 160° C. the solubility decreases steadily with increasing boron content, thus resembling the Pd-Pt isotherms. Since all the isotherms appear to converge at 27.5 at. per cent. boron, the solubility at this composition would be independent of temperature between

<sup>1</sup> Sieverts and Hagen, *Z. Phys. Chem.*, 1935, 174, 247.

<sup>2</sup> *Ibid.*, 1934, 168, 411.

0° and 800° C., thus resembling the hydride-forming metals like vanadium, decomposition of the hydride taking place at higher temperatures.

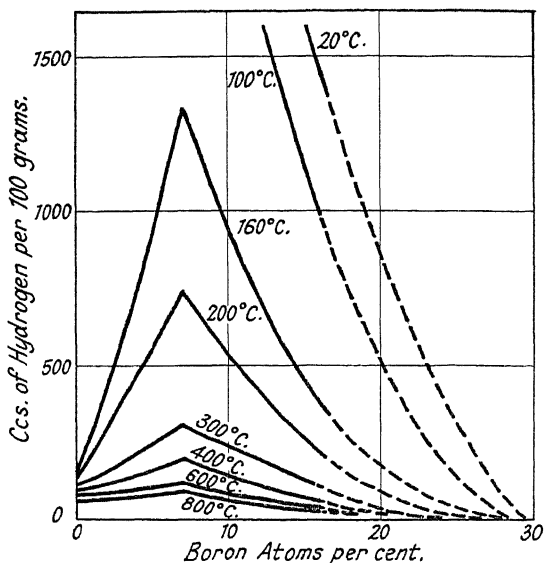


FIG. 140.—Solubility of hydrogen in boron-palladium alloys.

These palladium systems, whilst still somewhat obscure, illustrate the close connection between structure and solubility in a remarkable way.

### Effect of Dissolved Gases on the Properties of Metals.

Gases in solution nearly always increase the hardness and reduce the ductility of metals. In many cases failure in service may be traced to the effect of gases to which the metal has been exposed. In practice absorption of gas usually occurs during melting, or as the result of chemical or electrochemical action at the surface of the metal.

It has long been known that steel, from which the oxide scale has been removed by pickling in acid, is liable to become brittle, and Reynolds<sup>1</sup> showed in 1874 that this was due to the

<sup>1</sup> Reynolds, *Manchester Lit. Phil. Soc.*, 1874, 13, 93.

absorption of hydrogen by the metal. This phenomenon, which is of considerable practical importance, has been studied extensively. Pickling is usually carried out for about 5 minutes in 10 per cent. sulphuric acid solution at 50° C., but embrittlement may also result from pickling in other acids, in hot caustic soda, or in electrolytic baths in which the steel is made the cathode. Under all these conditions nascent hydrogen is produced at the surface of the metal, a proportion of which is absorbed. Neither nitric acid, nor electrolytic baths in which the steel is made the anode, induce brittleness. The effect is not permanent, and the metal recovers its normal properties almost completely on exposure to the atmosphere. The

TABLE 22

Material.	Per Cent. Elongation on 2 inches.		
	Before Pickling.	Acid Pickling.	Cathodic Pickling.
Mild steel .	38	—	14
" " .	50	40	35
Drill " .	22	—	7
Spring " .	51	3	3

time required for this to take place varies somewhat, and Langdon and Grossman<sup>1</sup> give the following figures for complete recovery :—

At room temperature . . . . .	3 days.
At 100° C. . . . .	2 hours.
At 150° C. . . . .	10 mins.

Immersion in boiling water for 10-30 minutes is usually sufficient, recovery being due to loss of hydrogen by diffusion.

The tensile strength, fatigue strength and impact values of the metal show very little change, and the embrittlement is chiefly apparent in the ductility or elongation values. Some typical results are summarised in Table 22.

<sup>1</sup> Langdon and Grossman, *Amer. Electrochem. S.*, 1920, 37, 543.

To eliminate the effects of recovery when the metal is exposed to air, Pfeil<sup>1</sup> carried out tests on annealed iron during pickling, with the results shown in Table 23. The effect of the absorbed hydrogen is most noticeable in the appearance of the fracture. Whilst in ductile metals fracture normally passes through the crystal grains, the brittle fractures induced by the presence of hydrogen occur either on the cleavage planes or along the crystal boundaries. In the tensile test, instead of a smooth cup and cone, the specimens show transverse cracks and the crystals are torn apart at the fracture. Mild steel broken under repeated stress, although giving a normal value, shows a fracture more like that of a quenched

TABLE 23.

Treatment.	Tensile Strength, tons/in. <sup>2</sup> .	Elongation on 1 inch, per cent.	Type of Fracture.
Before pickling . . .	18.34	62.5	Transcrystalline
During pickling at 25° C.	16.69	10.6	Intercrystalline
" " " 30° C.	17.5	22.5	"
" " " 50° C.	17.53	44.0	Transcrystalline
15 secs. after pickling .	18.44	60.5	"

and tempered steel. These observations indicate that the hydrogen enters the metal preferentially along slip planes or grain boundaries at the pickling temperature. At higher temperatures lattice diffusion is facilitated, and this probably explains the rapid recovery on warming.

The effect of pickling varies with different types of steel, although published results show a remarkable lack of agreement as to the effect of such factors as carbon content, or degree of cold working. Mild steels and alloy steels are least subject to pickling brittleness, which occurs most frequently in steels in their hardest state, as for example, in springs.<sup>2</sup>

<sup>1</sup> Pfeil, *Proc. Roy. Soc.*, 1926, 112, 182.

<sup>2</sup> Sutton, *J. Iron and Steel Inst.*, 1929, 119, 179.

Bardenheuer and Ploum<sup>1</sup> found that the degree of embrittlement was roughly proportional to the amount of hydrogen absorbed. The ductility is largely restored on removal of the hydrogen, although the original properties are never completely recovered. The removal of hydrogen is definitely accelerated by cold work, and heavily worked steel absorbs hydrogen less readily than metal which has only been lightly deformed.

A similar effect is found with some other metals and alloys. Lea,<sup>2</sup> for example, found a slight reduction in the elongation of nickel after cathodic pickling, but not with brass. Sutton and Taylor<sup>3</sup> studied the effect of various pickling treatments on the fatigue strength of Duralumin, and obtained the following results :—

Pickling Bath.	Reduction in Fatigue Limit.
2½ mins. in 10 % NaOH at 60° C.	31 %
2    „    „ 10 % HF, 10 % HNO <sub>3</sub> at 20° C. . . .	15 %
3    „    „ 10 % H <sub>2</sub> SO <sub>4</sub> + HF, wash in 50 % HNO <sub>3</sub>	6 %

In each case the reduction was much less after immersion in boiling water, or after a layer 0.0025 inch had been machined off the surface. These results are so similar to those obtained with steel that it seems certain that the explanation lies in hydrogen absorption.

The effect of hydrogen introduced into steel during melting has been established by the recent work of Drescher and Schäfer<sup>4</sup> on the effect of low temperature annealing. It is found that whilst the tensile properties of steels immediately after rolling may be quite satisfactory, the elongation and reduction in area values are sometimes low, but improve on standing. Annealing at 300°-400° C., which has no effect on the grain size or on the tensile strength, effects a marked im-

<sup>1</sup> Bardenheuer and Ploum, *Mitt. K. Wilhelm Inst. Eisenforsch.*, 1934, 16, 129.

<sup>2</sup> Lea, *Proc. Roy. Soc.*, 1929, 123, 171.

<sup>3</sup> Sutton and Taylor, *J. Inst. Met.*, 1934, 55, 149.

<sup>4</sup> Drescher and Schäfer, *Stahl u. Eisen*, 1935, 55, 914.

provement in elongation, as shown by the results given in Table 24 for a 0.18 per cent. C steel.

Drescher and Schäfer suggest that this is due to the diffusion out of the metal of hydrogen in excess of the saturated

TABLE 24.

Condition.	Tensile Strength, kg./mm. <sup>2</sup> .	Elongation, per cent.
Steel, as cast . . . . .	54	7
„ „ „ 60 hours at 100° C. . . . .	58	36
„ normalised . . . . .	61	18
„ „ 48 hours at 100° C. . . . .	61	49
Steel, as rolled . . . . .	59	18
„ „ „ 12 hours at 100° C. . . . .	59	28

solubility, and which is probably present as minute bubbles. Confirmation of this is given by Körber and Mehovar's<sup>1</sup> measurements of the hydrogen content of rail steels, given below, which show a definite correlation with the elongation values :—

Condition.	Tensile Strength, kg./mm. <sup>2</sup> .	Elongation, per cent.	Hydrogen, c.c./100 gms.
Immediately after rolling .	88.0	9.1	2.13
Heated 1 hour at 200° C. .	88.7	13.1	0.10
Stored 7 weeks . . . . .	89.0	12.9	0.10

Absorption of hydrogen by solid metals in contact with the gas in the molecular state only takes place at high temperatures, and examples of intercrystalline attack have already been given. Failure in service from this cause may be encountered in plant working at high temperatures. The hydride forming metals like tantalum and zirconium are particularly liable to embrittlement both by hydrogen and nitrogen when heated in

<sup>1</sup> Körber and Mehovar, *Mitt. K.W. Inst. Eisenf.*, 1937, 17, 89.



these gases, and show intercrystalline weakness. Many of these metals can only be prepared in a ductile form when the last traces of these gases are removed.

Metals prepared by electrodeposition are often characterised by extreme hardness, and considerable controversy has taken place as to whether this is due to absorbed hydrogen. In the electrodeposition of Ni, Cr, Fe, and Co considerable quantities of hydrogen are evolved at the cathode, some of which is undoubtedly absorbed by the metal. The amount of gas

TABLE 25.

## PROPERTIES OF ELECTRODEPOSITED METALS.

Metal.	Brinell Hardness of			Structure of Electrodeposit.
	Electrodeposit.	Fully Annealed.	Work Hardened.	
Chromium .	400-950	70	—	Indefinite
Nickel .	125	70	300	Columnar
	420-550	70	300	Indefinite
Cobalt .	164	86	—	Columnar
	380	86	—	Indefinite
Iron .	140	69	148	Columnar
	350	69	148	Indefinite
Copper .	40-62	40	102	Columnar
	130	40	102	Fibrous
	130-160	40	102	Indefinite

found by analysis may vary from 10 to 800 c.c. per 100 grams, depending on the conditions of deposition.<sup>1</sup> According to one view<sup>2</sup> the hardness of electrodeposits is due entirely to the presence of hydrogen in solution, and to its influence on the crystal lattice. In the light of recent work, however, this hypothesis is no longer tenable.

The variation in hardness obtained, when the conditions of deposition are altered, is illustrated by Macnaughton and Hotherstall's data,<sup>3</sup> given in Table 25. The hardness is in

<sup>1</sup> Macnaughton, *J. Iron and Steel Inst.*, 1924, 109, 409.

<sup>2</sup> Guillet and Cournot, *C. Rendus*, 1931, 192, 787.

<sup>3</sup> Macnaughton and Hotherstall, *Trans. Faraday Soc.*, 1935, 31, 1168.

many cases much greater than can be produced by cold work, and is generally increased by lowering the temperature of the bath, increasing the current density or the  $p_H$  value of the solution. All these factors tend to produce a very fine grained deposit. This is no doubt due to some extent to the obstruction to grain growth caused by the evolution of hydrogen at the surface, but the most important factor is the adsorption of colloidal basic compounds precipitated by the discharge of hydrogen ions. It is the presence of these non-metallic inclusions, and the resulting fine-grained structure, that is the real cause of the hardness. The soft deposits have a coarse columnar structure, whilst the hard deposits have either a very fine acicular form, or more often no discernible structure at all. On annealing at a high temperature *in vacuo*, the soft deposits develop large equiaxed crystals with clean boundaries, whilst the hard deposits show fine-grained structures with obvious non-metallic inclusions in the boundaries.

Guichard and his colleagues<sup>1</sup> have determined both the gas content and hardness of electrodeposits produced under various conditions of temperature and current density, but have been unable to find any correlation between hardness and gas content. Moreover, if the metal is out-gassed at successively higher temperatures, it is found that about 90 per cent. of the hydrogen can be removed before any softening is observed, and that softening continues after all the gas has been removed. It is therefore clear that although the presence of gas in solution may have some small effect on the mechanical properties of electrodeposited metals, their excessive hardness is not due to this cause.

The electrical properties of metals are also influenced by the presence of gas in solution. Changes in resistivity accompanying the absorption of hydrogen by palladium and tantalum have already been discussed, and similar effects are observed with other metals. The thermoelectric properties are particularly susceptible to the presence of dissolved gases. The

<sup>1</sup> Guichard, Clausman, Billon and Lanthony, *C. Rendus*, 1930, 190, 1417; 1931, 192, 623 and 1096; 1933, 196, 1660; *Chimie et Industrie*, 1934, 472.

thermal E.M.F. of platinum is increased by the presence of oxygen.<sup>1</sup> Franzini<sup>2</sup> gives the following values for the E.M.F. per °C. for couples of pure metals and hydrogen-saturated metals, the pure metal being electronegative in each case :—

Iron .	$0.705 \times 10^{-7}$ volt.
Platinum	$0.223 \times 10^{-7}$
Nickel .	$1.08 \times 10^{-7}$
Palladium	$174.5 \times 10^{-7}$

### Gases in Commercial Metals.

When a piece of metal prepared by a commercial process is heated for the first time *in vacuo*, a considerable quantity of gas is usually evolved. It is important to realise that such measurements do not necessarily give any information regarding the solubility of the gas or its ability to diffuse in the metal. The gas which is extracted may have been present

- (a) as blow holes or mechanical inclusions,
- (b) as an adsorbed layer on the surface,
- (c) in solution,
- (d) in combination.

As a rule, it is possible to determine the origin of the gas in any particular case, but a great deal of work has been published in which no attempt has been made to distinguish between these different sources. Although it is beyond the scope of this book to consider the problems of producing sound ingots or gas-free metals, some reference to the general principles involved in the determination of gases in metals may be made.

Vacuum extraction was first used by Graham<sup>3</sup> in 1867, and Troost<sup>4</sup> made some further measurements in 1873, but it is only in recent years that the subject has received serious attention. The usual method of determining the amount of gas present in a metal is to enclose the sample in a vessel which can be evacuated, and then measure the amount of gas given off at various temperatures. Treatment at any given

<sup>1</sup> Sivil, *Trans. Amer. Inst. Min. Met. Eng.*, 1931, 246.

<sup>2</sup> Franzini, *Reale Inst. Lomb. Sci. Let.*, 1933, 56, 1.

<sup>3</sup> Graham, *Proc. Roy. Soc.*, 1867, 16, 422.

<sup>4</sup> Troost, *C. Rend.*, 1873, 76, 482.

temperature results in an initial rapid evolution of gas, but this becomes slower and slower until it practically ceases. If the temperature is now raised, a further rapid evolution occurs, but again practically ceases after a short time. At each successively higher temperature more gas can be extracted. It is generally found that the whole of the gas present can only be removed in a reasonable time if the metal is actually melted.

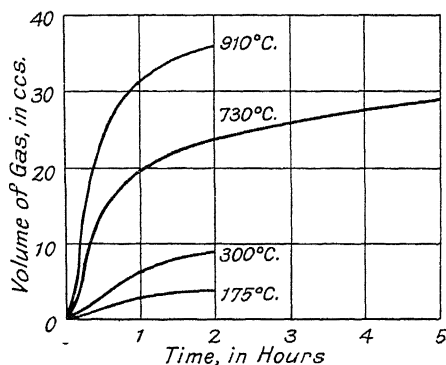


FIG. 141.—Rate of extraction of gases from electrolytic iron *in vacuo* at various temperatures.

[Hugues.]

Some typical degassing curves are given in Figs. 141 and 142. The removal of gases in this way depends on a process of

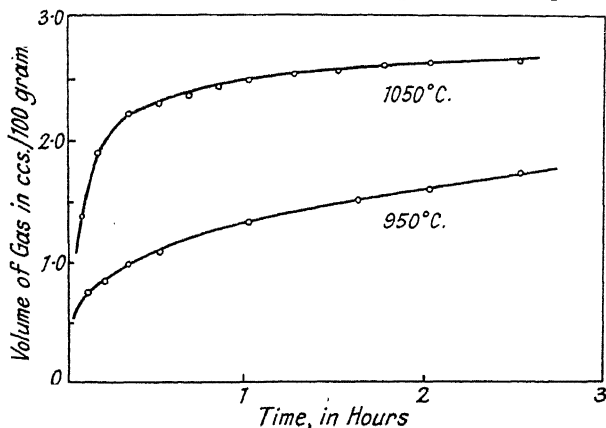


FIG. 142.—Rate of degassing 1.0 mm. diam. commercial nickel wire after degreasing with trichlorethylene.

diffusion, the rate of which is governed by the difference in concentration at the centre and at the surface of the metal.

As the quantity of gas in the metal becomes less, the relatively small difference in concentration results in very slow diffusion, particularly at moderate temperatures. The very high temperature coefficient, characteristic of all gas-metal diffusion processes, accounts for the sudden increase in the rate of evolution each time the temperature is raised. Above the melting-point diffusion is aided by the motion of the liquid metal.

In the case of a gas in true solution, such as hydrogen in nickel, it has been shown<sup>1</sup> that the rate of extraction at a given temperature follows Fick's diffusion law. For the migration of a gas within a metal this may be written

$$\frac{dc}{dt} = \Delta \frac{d^2c}{dx^2} \quad (33)$$

This can be applied most conveniently if the specimen is in the form of a round wire, when the equation becomes

$$\frac{1}{\Delta} \frac{\partial c}{\partial t} = \frac{\partial^2 c}{\partial r^2} + \frac{1}{r} \frac{\partial c}{\partial r}.$$

A particular solution of this equation is

$$q = 2c\Delta/r \sum_{a=1} e^{-} \quad (34)$$

where

$q$  is the rate of gas evolution from the wire in c.c./cm<sup>2</sup>./sec. ;

$c$  the initial concentration of gas in cubic centimetres at N.T.P. in 1 c.c. of metal ;

$r$  the radius of the wire in cm. ;

$t$  the time of degassing in seconds ;

$\Delta$  the diffusivity constant of the gas in the metal, and

$\lambda_a = \xi_a/r$ , where  $\xi_a$  are the zeros of the Bessel function  $J_0(\lambda)$ .

Two assumptions are made in the derivation of equation (34); namely, that at the beginning of the process the gas is evenly

<sup>1</sup> Euringer, *Z. Physik*, 1935, 96, 37 ; Smithells and Ransley, *Proc. Roy. Soc.*, 1936, 155, 195 ; Norton and Marshall, *T. Amer. Inst. Min. Met. Eng.*, Feb., 1932.

distributed throughout the metal, which is assumed to be homogeneous, and that the concentration of gas at the surface is zero. The latter implies that the evaporation of gas from the surface is rapid in comparison with the diffusion to the surface. This is probably true for most gas-metal systems, but there is evidence that in some the rate of removal of gas from the surface is a controlling factor in the desorption process.

Equation (34) may be written

$$\log q = \log 2c\Delta/r + \log \{e^{-5.8 \Delta t/r^2} + e^{-30.5 \Delta t/r^2} + e^{-75.0 \Delta t/r^2} + \dots\} \quad (35)$$

At higher values of  $t$ , depending on the numerical value of  $\Delta/r^2$ , the series very rapidly converges, and equation (35) may ultimately be written

$$\log q = \log 2c\Delta/r - 5.8\Delta t/r^2 \quad (36)$$

since terms of the series other than the first may then be neglected. This is by far the most useful form of the equation.

If  $\Delta$  remains constant, as in the degassing of a wire at a constant temperature, we have for high values of  $t$

$$\log q = A - Bt.$$

The logarithm of the rate of gas evolution plotted against the time should therefore give a straight line. The change in slope of this line with temperature will be directly proportional to the variation of the diffusivity constant with temperature. Some examples of the application of these equations are given later.

### Apparatus and Methods of Measurement.

The determination of the gas content below the melting-point is usually carried out in an apparatus similar to that used for solubility determinations, shown in Fig. 96. In this case, however, the gas evolved is pumped into an analytical system where its composition can be determined. The metal, from 10 to 100 grams in weight, may be in one piece or broken into fragments. If the total surface of the sample is increased it facilitates the extraction of the gas, but also increases the amount of gas present as an adsorbed layer. This may be large

in comparison with the total gas content of the metal itself. Steinhäuser<sup>1</sup> has emphasised the importance of this factor. Measurements, made by different workers, of the quantity of gas that can be extracted from commercial aluminium vary from 1 to 30 c.c./100 grams of metal. This has been attributed to differences in the methods of manufacture of the metal. By carefully cleaning the surface of his samples, Steinhäuser obtained consistent values of about 0.2 to 0.7 c.c./100 grams, and attributed the high values obtained by others to surface contamination. Even if the samples are washed in benzine and alcohol, it is important that these reagents should be free from grease in solution, which might leave a film on the metal. Another source of error lies in the difficulty of completely freeing the apparatus itself from gas before beginning the determination. If the metal is available in the form of wire or strip there are considerable advantages in heating by high frequency currents, in which case the containing vessel itself can be kept cold, and does not contribute to the gases collected. The form of apparatus shown in Fig. 51, designed for diffusion measurements, is equally suitable for gas determinations, with the same analytical system. The sample, in the form of a coil of wire or a cylinder of sheet metal, is suspended by fine tungsten wires in a bulb of about 80 mm. diameter. It is quite easy to maintain the temperature constant within the accuracy of the pyrometer reading by means of the high frequency coil, and the bulb can be kept cold by an air blast.

This method is very convenient for studying the effect of surface contamination. Consistent results can be obtained with wire if it is washed in trichlorethylene to remove grease. For example, determinations on the same sample of nickel wire carried out at various times during a period of two years gave values for the total gas content which only varied between 2.34 and 2.64 c.c./100 grams. In addition to surface contamination of the kind removed by washing, gas may also be derived from impurities worked into the surface during manufacture. An

<sup>1</sup> Steinhäuser, *Z. Metallk.*, 1934, 26, 136.

estimate of the amount of gas derived from this source may be made by comparing the amount of gas obtained from samples of different diameter. In the case of commercial nickel wire Smithells and Ransley<sup>1</sup> found that about half of the total gas came from these surface impurities.

Similar methods are used for extracting gases from metals above their melting-points. Greater precautions must be taken to degas the crucible containing the metal and to ensure that gas is not liberated by reactions between the metal and the material of the crucible. This method, which is generally known as the vacuum fusion, or hot extraction, method of gas analysis, is associated with the name of Oberhoffer, who developed it largely for the determination of oxygen in steel. Various forms of apparatus have been used with slight modifications, the usual form being that employed by the Bureau of Standards. The history of the development of this process has been given by Hessenbruch,<sup>2</sup> and for full details of the method at present in use the reader should consult the original paper by Vacher and Jordan.<sup>3</sup> For determinations of oxygen, hydrogen and nitrogen in steels the sample is melted in a graphite crucible in a high-frequency induction furnace, and the gases evolved continually extracted by a mercury diffusion pump. Oxides, with the possible exception of alumina, are completely reduced and removed as CO. The gases, which are collected in a reservoir, are circulated through suitable absorbents and determined gravimetrically. The CO and hydrogen are first oxidised by passing over hot copper oxide, the CO<sub>2</sub> and H<sub>2</sub>O absorbed, and the volume of the residual nitrogen determined. The method gives results accurate to about 0.002 per cent. by weight for oxygen and nitrogen, provided certain elements such as manganese are not present in excessive quantities.

A new method of extracting gases from solid metals has

<sup>1</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1936, 155, 195.

<sup>2</sup> Hessenbruch, *Z. Metallk.*, 1929, 21, 46.

<sup>3</sup> Vacher and Jordan, *Bur. Standards J. Res.*, 1931, 7, 375; see also Thompson, Vacher and Bright, *Amer. Inst. Min. Met. Eng.*, Tech. Pub. No. 758 (1936).



recently been proposed by Moreau, Chaudron and Portevin.<sup>1</sup> The sample is made the cathode in a discharge tube operating at 150,000 volts with a current of about 5 milliamps. The gas which is evolved under the influence of the discharge is continuously pumped away. The removal of the gas is attributed to the effect of surface ionisation and removal of the ions by the electric field. The metal is not appreciably heated by the discharge, and rest periods of 24 hours are necessary to allow fresh gas to diffuse to the surface. The total quantities of gas obtained by this method are from 50 to 100 times as great as those obtained by the hot extraction methods. Further experience is required before these results can be accepted with confidence, and particularly confirmation that the gas originates entirely from the metal.

The total quantity of gas that can be extracted from commercial metals by heating *in vacuo* is usually between 1 and 20 c.c./100 grams of metal. With copper and aluminium the gas is largely hydrogen, but carbon monoxide is the chief constituent in iron and nickel. Since, as we have seen, the compound gases can neither dissolve nor diffuse as such in metals, their origin under these conditions is of some interest. The most obvious explanation, which has proved to be the correct one, is that they result from reactions between constituents present in the metal. The evidence for this view is cumulative, but the first definite proof that the CO derived from steel is due to reaction between the dissolved oxide and carbide in the metal was given by Oberhoffer and Piwowarsky.<sup>2</sup> They showed that only a very small quantity of gas was obtained on dissolving steel in mercuric chloride in the cold, but a much larger quantity when the metal was heated *in vacuo*. Smithells and Ransley<sup>3</sup> studied the desorption of carbon monoxide from nickel and found that it was controlled entirely by the rate of diffusion of the carbon in the metal. The temperature coefficient of the rate of desorption was identical with that for the diffusion of carbon through nickel. Moreover,

<sup>1</sup> Moreau, Chaudron and Portevin, *C. Rend.*, 1935, 201, 212.

<sup>2</sup> Oberhoffer and Piwowarsky, *Stahl u. Eisen*, 1922, 42, 801.

<sup>3</sup> *Loc. cit.*

when no more CO could be extracted by vacuum treatment, a further quantity could be obtained after the surface had been lightly oxidised, the amount of oxygen present in the metal being insufficient to remove the much larger quantity of carbon. Methane and ammonia, which are obtained from aluminium, presumably have their origin in the carbides and nitrides present in the metal. The values for oxygen in steel obtained by the hot extraction method correspond to the oxygen present as reducible oxides, such as those of iron and manganese, whilst the oxides of titanium and aluminium are not completely decomposed. The results of gas analysis therefore require careful interpretation, and it must not be assumed that the gases found are necessarily present in the metal in solution. The extraction of gases from commercial metals has been studied from two different points of view. Firstly, in order to understand the origin of unsoundness in ingots, with a view to modifying the metallurgical processes involved, and, secondly, in order to obtain metals which will not evolve gas when heated in vacuum, for the manufacture of such devices as thermionic valves, cathode ray tubes, etc. Some of these investigations may be summarised to illustrate the nature of the results obtained.

*Nickel.*—The gas extracted from cathode nickel and Mond nickel pellets is mainly hydrogen and CO.<sup>1</sup> Mond pellets may contain as much as 100 c.c./100 grams, about 80 per cent. of which is CO, whilst electrodeposited nickel contains only about 10 c.c./100 grams, 80 per cent. of which is hydrogen. Nickel wire or sheet prepared by remelting either of these types of nickel contains, as a rule, much less gas, 80 per cent. of which is CO.<sup>2</sup> A typical analysis of the gas extracted at progressively higher temperatures is given in Table 26 (p. 206).

Hydrogen, which diffuses readily in nickel, is quickly extracted at low temperatures; CO, however, is only removed by prolonged treatment at high temperatures. The rate of

<sup>1</sup> Hessenbruch, *Z. Metallk.*, 1929, 21, 46.

<sup>2</sup> Smithells and Ransley, *Proc. Roy. Soc.*, 1936, 155, 195; Norton and Marshall, *T. Amer. Inst. Min. Met. Eng.*, Feb., 1932.

evolution at 950° C. and 1050° C. is shown in Fig. 143, the full lines being the theoretical curves for equation (35) on page 201. From the slopes of these curves the values of the diffusivity constants obtained are

$$\begin{aligned}\Delta_{950^{\circ}\text{C.}} &= 4.0 \times 10^{-8} \text{ cm}^2/\text{sec.} \\ \Delta_{1050^{\circ}\text{C.}} &= 14.0 \times 10^{-8} \quad ,,\end{aligned}$$

The rate of extraction is therefore increased 3.6 times by raising the temperature from 950° C. to 1050° C. These diffusivity constants, and also the temperature coefficient, are identical

TABLE 26.

EVOLUTION OF GAS AT DIFFERENT TEMPERATURES FROM 1 MM. DIAM.  
NICKEL WIRE CLEANED IN TRICHLOROETHYLENE.

Time of Heating.	Temperature, °C.	Gas in c.c./100 gms.			Total.
		CO <sub>2</sub> .	H <sub>2</sub> .	CO.	
20 mins.	750	0.08	0.23	0.36	0.67
20 „	850	0.03	0.03	0.33	0.39
20 „	950	0.03	0.03	0.54	0.60
20 „	1050	0.05	0.03	0.45	0.53
20 „	1150	0.03	0.11	0.13	0.27
		0.22	0.43	1.81	2.46

with those for the diffusion of carbon in nickel, and indicate that the evolution of CO is controlled by diffusion of carbon to the surface of the metal.

An alternative method of investigating the course of degassing is to subject the wire to heat treatment for various periods of time, either in hydrogen or vacuum, and then determine the amount of gas remaining in the metal. In this way a curve of the kind shown in Fig. 144 is obtained. No difference is shown by samples treated in hydrogen or vacuum. Heating in hydrogen does introduce more hydrogen into the metal, but owing to its high rate of diffusion it is almost entirely removed by baking at 450° C.

Nickel which has been freed from gas by vacuum treatment

does not reabsorb gas on exposure to the atmosphere, unless it is definitely oxidised, when a further quantity of CO will be obtained.

*Aluminium.*—Aluminium is very liable to give unsound castings, and the difficulty of avoiding pinholes has led to extensive investigation of the gases in commercial aluminium,

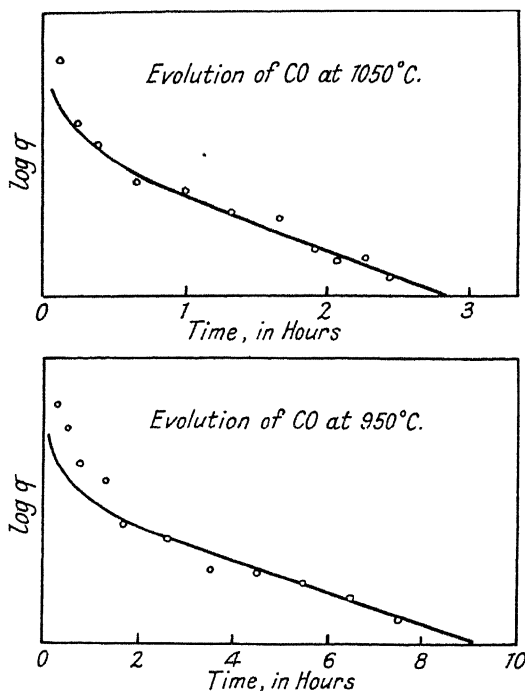


FIG. 143.—Rate of evolution of CO from commercial nickel *in vacuo*. Full lines show theoretical curve.

and their elimination. There are considerable variations in the amount of gas found by different workers, but general agreement that the gas consists mainly of hydrogen (60-90 per cent.), the remainder being either CO or CH<sub>4</sub>. The total quantities reported<sup>1</sup> vary from about 2 to 30 c.c./100 grams,

<sup>1</sup> Hessenbruch, *loc. cit.*; Riebeling, Thesis, Aachen, 1929; Braun, *Metallwirtsch.*, 1932, 11, 459; Villachon and Chaudron, *C. Rend.*, 1929, 189, 324; Kolobnev, *Zvetnye Metalli*, 1936, 5, 110.

and Hessenbruch, and Villachon and Chaudron both found between 10 and 30 per cent. CO in addition to hydrogen. Steinhäuser<sup>1</sup> has criticised these results, which he attributes largely to surface gas, and finds, after careful washing of the surface, a total of only 0.5-0.6 c.c., composed of 70 per cent. hydrogen and 30 per cent. CH<sub>4</sub>, CO being entirely absent. If the surface is contaminated with grease the proportion of CH<sub>4</sub> is increased, and CO and CO<sub>2</sub> are also found. Moreau<sup>2</sup> and his associates reported very much larger quantities of gas extracted by the discharge method, amounting to as much as 150 c.c./100 grams, 30 per cent. of which was CO, together

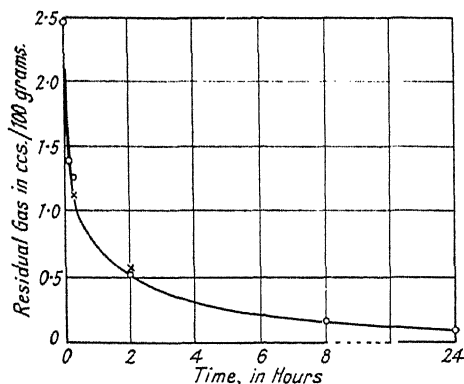


FIG. 144.—Effect of furnace treatment on gas content of commercial nickel wire.

○ After heating at 950° C. in hydrogen.

× „ „ 950° C. in vacuo.

with a small amount of nitrogen due to the presence of nitride in the metal.

The origin of the hydrogen in aluminium was shown by Hanson and Slater,<sup>3</sup> and independently by Claus,<sup>4</sup> to be due to the decomposition of water vapour by molten aluminium. Owing to the very small solubility in the solid

metal, the hydrogen is liberated during solidification, and remains in the metal as small bubbles or pinholes. A higher casting temperature therefore results in a larger evolution of gas and an ingot of lower density. Since aluminium is always melted under conditions where gas can be absorbed, the melt is usually degassed by treatment either with nitrogen or a volatile chloride. Hydrogen may also be introduced by using scrap metal which

<sup>1</sup> Steinhäuser, *Z. Metallk.*, 1934, 26, 136.

<sup>2</sup> Moreau, Chaudron and Portevin, *C. Rend.*, 1935, 201, 212.

<sup>3</sup> Hanson and Slater, *J. Inst. Met.*, 1931, 46, 187.

<sup>4</sup> Claus, *Z. Metallk.*, 1929, 21, 268.

has undergone corrosion, the nascent hydrogen produced being absorbed by the metal.<sup>1</sup>

*Copper.*—Molten copper absorbs both oxygen from the air, and hydrogen from the furnace gases, or from the decomposition of water vapour. Whilst on freezing the oxygen is precipitated as solid cuprous oxide, the hydrogen is thrown out of solution. This results in a reaction between hydrogen and cuprous oxide, and the steam so formed remains entrapped in the metal. The molten copper is usually deoxidised with wooden poles, so as to leave about 0.05-0.06 per cent. of oxygen in the metal. The evolution of steam then just balances the natural shrinkage of

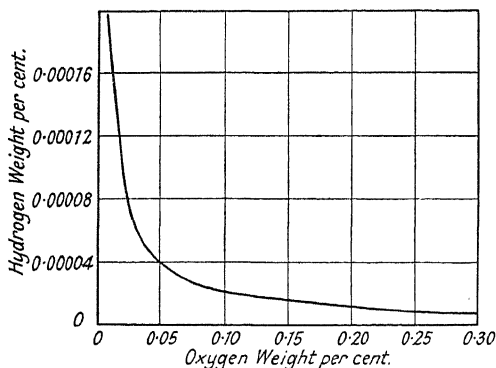


FIG. 145.—Variation of hydrogen solubility in molten copper with oxygen content.

[Allen.

the metal, and a pipe is avoided. In principle, this is very similar to the manufacture of rimming steel, where the evolution of CO produces the same effect.

According to Allen<sup>2</sup> the solubility of hydrogen in copper is reduced by the presence of oxygen, as shown in Fig. 145, and the difficulties experienced if the oxygen content is reduced below 0.05 per cent. may be due to this cause. Sulphur dioxide is also absorbed by molten copper, giving rise in the solid metal to both  $\text{Cu}_2\text{O}$  and  $\text{Cu}_2\text{S}$ , which may again react to give  $\text{SO}_2$ .

<sup>1</sup> Hanson and Slater, *J. Inst. Met.*, 1931, 46, 187.

<sup>2</sup> Allen, *ibid.*, 1930, 43, 81.

A typical analysis <sup>1</sup> of the gases obtained by vacuum extraction gave about 2 c.c./100 grams, consisting of 60 per cent. SO<sub>2</sub>, 20 per cent CO, and 14 per cent. H<sub>2</sub>. The alloys of copper with zinc and tin usually contain less hydrogen.<sup>2</sup> The presence of SO<sub>2</sub> is also less likely to lead to unsoundness, since the oxygen is largely present as the oxides of tin or zinc which do not react with cuprous sulphide.<sup>3</sup>

*Zinc.*—The gas extracted from electrodeposited zinc is almost pure hydrogen. The quantity obtained depends on the conditions of deposition. Röntgen and Möller <sup>4</sup> found that the hydrogen content increased in direct proportion to the square root of the current density, and also increased with the temperature of the bath. On the other hand, Burmeister and Schloetter <sup>5</sup> found the opposite effect, the hydrogen content being chiefly dependent on whether the electrolyte was stirred (increasing the H<sup>+</sup> concentration) or kept still. The amount of hydrogen found in both these investigations was between 20 and 60 c.c./100 grams.

*Iron and Steel.*—The gases extracted from steel consist chiefly of hydrogen and the oxides of carbon. The latter are derived from reactions between carbon and reducible oxides, chiefly those of iron and manganese, present in the metal. Guillet and Roux <sup>6</sup> found about 30 c.c./100 grams, of which 40 per cent. was CO and 40 per cent. hydrogen. Smaller quantities of nitrogen derived from nitrides are also found. The oxygen and nitrogen content of steels varies with different qualities, some representative values being given on the opposite page.<sup>7</sup>

*Tungsten and Molybdenum.*—Only very small quantities of gas are obtained from these metals on heating *in vacuo*. This

<sup>1</sup> Hessenbruch, *loc. cit.*

<sup>2</sup> Tyrie, *Metal Ind.*, 1934, 44, 461.

<sup>3</sup> Röntgen and Schweitzke, *Z. Metallk.*, 1929, 21, 117.

<sup>4</sup> Röntgen and Möller, *Metallwirtsch.*, 1932, 11, 685.

<sup>5</sup> Burmeister and Schloetter, *ibid.*, 1934, 13, 115.

<sup>6</sup> Guillet and Roux, *Rev. Met.*, 1929, 26, 1.

<sup>7</sup> Swinden, *Foundry Trade J.*, 1936, 55, 418; Stevenson, *Ind. Chemist*, 1934, 10, 307; Eilender, von Bohlen and Meyer, *Arch. Eisenhut.*, 1933, 7, 493.

is probably due to the fact that they are repeatedly annealed in hydrogen during manufacture. The total quantity of gas obtained at 1760° C. corresponds to about 0.05 and 0.5

Type of Steel.	Weight, Per Cent. O <sub>2</sub> .	Weight, Per Cent. N <sub>2</sub> .
Crucible steel . . .	0.005	.004-.007
Open hearth . . .	0.025	.004-.007
Basic rimming . . .	0.10	—
Bessemer . . .	—	.012-.018
Vacuum melted M.S. . .	.001-.01	.0005-.003

c.c./100 grams of tungsten and molybdenum, respectively. In both cases the gas is composed of 50-60 per cent. N<sub>2</sub>, 30-40 per cent. CO, with a small amount of hydrogen.<sup>1</sup>

<sup>1</sup> Norton and Marshall, *T. Amer. Inst. Min. Met. Eng.*, Feb., 1932.





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